Sediment trace elements in lake cores as indicators of rural land use change in six selected New Zealand lakes

---

A thesis

submitted in partial fulfilment

of the requirements for the Degree of

Master of Water Resources Management

at

Lincoln University

by

Lughano Mwenibabu

Waterways Centre for Freshwater Management

Lincoln University

2020

Abstract of a thesis submitted in partial fulfilment of the requirements for the Degree of Master of Water Resources Management.

Sediment trace elements in lake cores as indicators of rural land use change in six selected New Zealand lakes

by

Lughano Mwenibabu

Ongoing concerns of water quality degradation in New Zealand lakes in agricultural catchments, mean that it is important to develop an understanding of both past and present conditions of lake water quality. Lake sediments can provide reliable natural records of catchment land use change, and can be used to assess the long term impacts of anthropogenic activities on lakes. Large scale studies of lake sediment cores, such as the New Zealand-wide Lakes380 research programme, can help to inform future water management policies or strategies to improve water quality in lakes. Such studies involve comprehensive collection of chemical, biological and physical parameters, which are collectively very expensive to determine. However, a subset of key environmental land use indicators, which can be more affordable to determine, may be identified from this work.

The purpose of this study was to assess the potential for using trace elements signatures in lake sediment cores, as indicators of rural land use change. Sediment cores were collected from each of the six New Zealand lakes found in various agricultural land use settings: two lowland lakes (Lake Tutaeinanga and Lake Ngāpouri), two coastal lakes (Lake Moawhitu and Lake Forsyth/Wairewa) and two highland lakes (Lake Pearson and Lake Heron). The cores were dated using pollen analysis methods to identify the prehuman period and major human settlement periods (Māori and European settlements).

The study determined the concentrations of trace elements that are commonly used in New Zealand agriculture (arsenic (As), cadmium (Cd), copper (Cu) and zinc (Zn)), and other elements that may provide supporting information on the sources and distribution of the agriculturally-relevant trace elements. The trace elements were digested and analysed using the inductively coupled plasma - optical emission spectrometry (ICP-OES) technique. The study also determined the enrichment factors to differentiate trace elements originating from anthropogenic activities and those from prehumen conditions. The trace elements concentrations and enrichments were linked to the history of land use changes in the respective lake's catchments.

The results of the study has shown that P, Cu and Zn showed similar enrichment in recent sediments across most of the lakes studied, and they related to rural land use activities (application of fertilizer and agrichemicals) in the period of European settlement. Cd showed similar recent enrichment in Lake Tutaeinanga, Lake Pearson and Lake Heron, but not in super-eutrophic lakes (Ngāpouri and Moawhitu and some cores in Lake Forsyth/Wairewa), where Cd concentrations may have been affected by biogeochemical processes. Arsenic showed similar

enrichment to P, Cu and Zn in Lake Forsyth, Lake Pearson and Lake Heron. The distribution of arsenic in Lake Tutaeinanga and Lake Ngāpouri was affected by volcanic and geothermal activities prevalent in the catchment. Other trace elements, such as Pb, were more indicative of road runoff affecting recent sediments, and Fe and Mn were determined largely to understand their effects on the distribution of other elements.

The studied trace elements also identified impacts related to land use activities associated with Māori settlement in New Zealand, which were largely attributed to enhanced soil erosion due to clearing land. This effect was also evident, and generally to a great degree, in the European settlement era in some of the lakes.

Keywords: land use change, trace elements, sediments, agriculture, water pollution, paleolimnology, water quality, enrichment factors

Acknowledgements

I would like to express my gratitude to the Ministry of Foreign Affairs and Trade (MFAT) for the New Zealand scholarship that has enabled me to study my Masters of Water Resources Management. This research would have not been possible without your scholarship. Also to the New Zealand scholarship team here at Lincoln University: Sue Bowie, Jayne Borrill and Mandy Buller, thank you for your support and for making my life confortable during my study period.

I am highly grateful to my main supervisor Professor Jenny Webster-Brown for the great support accorded to me during my entire project period despite your busy schedule. Your advice, motivations, time, perseverance, direction, influence and corrections are highly appreciated. You have been a big influence on me and you opened my eyes beyond my expectation each time I approached you. God bless you richly. I am also grateful to my co-supervisors Dr Sean Waters from (Cawthron Institute) and Dr Crile Doscher. Thank you for your advice, corrections and your time. Dr Sean, thank you for making sure I had everything I needed from Lakes380 project.

To the Lakes380 project team members, Susie Would (Cawthron Institute), Marcus Vandergoes (GNS) Jamie Howarth (VUW), Lizette Reyes (GNS) and all other team members, thank you for your guidance and support and for providing me with the necessary data for my research. Your commitment to help me with my research was impeccable.

I am thankful to the Waterways staff and office colleagues at Waterways for the support rendered to me throughout my programme of study. A special mention to John Ravell, the Waterways lab manager for assisting me with my lab work.

Many thanks to all my friends and family, both in Malawi and here at Lincoln for their support and care. I am also grateful to my wife, Thelma Chirwa, for her support during the study period and for bearing with me for being away from her during the whole study period. I am also grateful to my mum and dad, for their support and prayers throughout my entire life.

Above all I am grateful to God for giving me his life and grace to move on in this life.

Table of Contents

List of Tables

List of Figures

Chapter 1

Introduction

1.1 Background

Lakes provide important ecosystem services that support life on earth. These services include recreation, water supply (for irrigation, industrial and domestic uses), cultural and aesthetics, habitation for aquatic life, hydroelectric power generation and the provision of food and aquaculture services. Although lakes have historically supported most of these services, their ability to continue doing so is being heavily threatened by anthropogenic activities (UNEP, 1996; Vitousek et al., 1997). Man's activities have replaced the pristine landscape with new land uses that degrade water quality and reduce water quantity in lakes.

The major land use activities that contribute to these problems are agriculture, urbanisation and industrialisation. These activities generate more pollutants and create a bare pasture ground and hard surfaces leading to increased amounts of runoff. As a result, more sediments and contaminants such as nutrients, microorganisms, trace elements, hydrocarbons and other chemicals accumulate in lakes. According to UN WWP (2003) there are over two million tons of sewage, industrial and agricultural waste being discharged into water bodies every day. The effects of land use continue to escalate at an alarming rate due to population growth, economic development and change of social preferences (UN World Water Assessment Programme, 2019).

Lakes are particularly affected by what happens in the whole catchment because they are at the receiving end of the catchment (Burt et al., 1993; P. Johnes & Heathwaite, 1997). They act as sinks for catchment waterways and therefore become relevant sentinels in catchment water management. Lake studies provide relevant information that can be used to control land use activities in the whole catchment (Foy et al., 1982; Moss et al., 1996). According to P. J. Johnes (1999), sustainable management of catchment must be underpinned by understanding lakes' functions and the origins of land use changes in the catchment.

1.1.1 Lake water quality management

Currently, many lakes and other water bodies in the world have been graded as unfit for many purposes (Ricciardi & Rasmussen, 1999; UN WWAP, 2019; Vitousek et al., 1997). In New Zealand's lakes, water quality is in a variable state. According to a freshwater report by (MfE, 2017), lakes with catchments that are predominantly covered by urban or agricultural land uses are typically associated with poor water quality, while those that have natural land cover are associated with good water quality. The major concern in regions that are dominated by agriculture, such as Canterbury, Waikato, and Southland, has been pollution of lakes by rural land use activities. Agricultural intensification and land use conversion from sheep and beef farming to dairy farming have increased amount of pollutants entering into lakes and waterways (MfE, 2019).

To offset the effects of land use changes on lakes' water quality, different management initiatives are being trialled worldwide. These management initiatives are targeting the restoration of lakes' healthy ecosystems.

According to OECD (2001) water quality in most lakes and other water bodies continues to decline despite these initiatives put in place by governments and other organisations. These initiatives are failing because they often focus on water quantity, water allocation and water-use efficiency issues, leaving waste water management issues unattended to (UN WWAP, 2019). Also most management initiatives target managing point source pollution, but fail to manage non-point source pollution such as diffuse runoff from agricultural land (OECD, 2001).

In trying to form new strategies and plans governing both land use and water quality management, a better long-term understanding is needed of how lakes respond to changes in catchment land use. Long-term lake monitoring programmes can be used to establish the impacts of human-induced land use changes. However, in New Zealand, lake monitoring started in the 1980s while most human land-use alteration occurred about 200 years ago when Europeans arrived in the country (R. Taylor & Smith, 1997). Natural historical records such as lake sediment cores are therefore necessary to provide a long-term record of human-induced land use changes in New Zealand (Smol, 2002).

Lake sediments are natural archives that can be used to provide information on the current and past water quality and aquatic biodiversity and their response to land use changes. In some previous studies, lake sediments have also been used to study the effects of climate change (Abbott et al., 2003; Gudasz et al., 2010; Schmidt et al., 2002). Large-scale studies of lake sediment cores, such as the New Zealand-wide Lakes380 research programme, can lead to a better understanding of how future management policies or strategies can be developed to reduce the effects of land use changes on lakes. Such studies involve comprehensive collection of chemical, biological and physical parameters, which are collectively very expensive to determine. However a subset of key environmental land use indicators may be identified from this comprehensive information.

1.2 The Lakes380 project

The Lakes380 research programme is a five-year programme that aims to solve a data limitation problem by assessing the health and recent history of 380 lakes in New Zealand. New Zealand has about 3800 lakes that are above one hectare in surface area, so this project targets 10% of those lakes. The programme uses a combination of both traditional environmental techniques and more recent innovations such as environmental DNA (eDNA) and high-resolution core scanning, to characterise the current lake health and explore the causes and rates of change in state over the past 1000 years.

Ultimately, the Lakes380 programme will provide baseline information of lakes' conditions which will inform future management policies and strategies on the national scale. The programme is being funded by the Ministry of Business, innovation and employment (MBIE) and is being carried out by GNS science and Cawthron Institute. This research project has been done in collaboration with the Lakes380 project.

1.3 Research aim and objectives

The main aim of this research project was to assess the potential for using trace element signatures in lake sediment cores, as indicators of rural land use change in catchments, using six New Zealand lakes. The study

intended to potentially identify relatively simple and inexpensive indicators of past land use change, which can be used by local or regional authorities to understand and better manage the impacts of those changes on lake environments.

1.3.1 Specific objectives

1. To collect or access sediment cores from Lake Pearson, Lake Heron, Lake Forsyth (Te Roto Wairewa), Lake Tutaeinanga, Lake Ngāpouri (Opouri) and Lake Moawhitu (in collaboration with the Lakes380 project).

2. To determine the concentrations of trace elements used in agriculture (such as arsenic, cadmium, copper, phosphorus and zinc) as well as those that may provide supporting information on the sources and distribution of the agriculturally-related trace elements that as a function of depth in these cores.

3. To determine enrichment factors (EF) and modified pollution index (MPI) which are applied to differentiate the trace elements originating from anthropogenic activities and those from natural means.

4. To assess whether the trace element profile in lake sediment cores identifies periods of historic land use change in the catchment

Chapter 2

Literature Review: Land Use and Lake Environments

2.1 Land use change and its environmental effects

The world is now experiencing the highest rate of man's alteration of land surface cover than ever before (Shaghla et al., 2018). Economic development growth, population growth and change of social preferences are among the main factors accelerating this unprecedented change of land cover/land use. Land cover or land use changes have direct impacts on the ecosystem services provided by lakes, including loss of biotic diversity, degradation of water quality and reduction of water quantity (Rodda & Shiklomanov, 2003).

Land surface cover can be changed by either natural events or anthropogenic activities. Natural events that alter land cover encompass floods, earthquakes, climate fluctuations and ecosystem natural changes. On the other hand, anthropogenic land uses such as agricultural development, industrialisation and urbanisation have also contributed to more land cover change (FAO, 2017).

2.1.1 Urbanisation and industrialisation

Urbanisation means movement of people from rural areas to settle in cities and towns (Cambridge Dictionary, 2008). This entails establishment of more buildings, roads and services to support the increasing population. Industrialisation is when an economy transforms from depending on primary production such as agriculture to more complex processes such as manufacturing units (Cambridge Dictionary, 2008). Both urbanisation and industrialisation result in the creation of impermeable surfaces and generation of more waste and pollutants (Almeida et al., 2007; Juma et al., 2014). The impermeable surfaces created reduce leaching of water into ground and increase surface runoff of water into waterways and lakes (Teng et al., 2011). The surface runoff carries industrial contaminants such as trace elements, detergents, pharmaceuticals and hydrocarbons as well as pollutants from homes and urban areas, such as nutrients, pathogens, sediments and trace metals from roofs, car tyres and car brakes, into storm water networks and eventually into waterways and lakes (Davis et al., 2010). In New Zealand, most urban waterways are polluted by excessive nutrients, sediments, pathogens and trace elements, which have caused some water bodies to be poorly graded for purposes such as swimming and ecosystem health (MfE, 2019).

2.1.2 Agricultural development

Agriculture alone contributes to more land use changes than urbanisation and industrialisation combined (FAO, 2017). Population growth and change of social preferences have increased the demand for more food and led to more food diversity (FAO, 2017). This in turn has led to both agricultural intensification and the expansion of land to produce more food, consequently leading to removal of natural forests and shrubs and the use of more fertilisers, pesticides and chemicals to produce more food per unit area (Shaghla et al., 2018).

In less than 1000 years, New Zealand has seen a tremendous change in land cover from densely forested islands, to a highly farmed country (MfE, 2019). The creation of farms involved clearing natural land cover and introducing chemicals such as fertilisers and pesticides. In the past two decades, the country has also seen conventional agricultural land use change in dry regions from sheep and beef farming to dairy farming, which produces more pollutants and requires more use of fertilisers. For instance, in the regions of Otago, Canterbury and Southland, dairy herds increased by 70% from 1994 to 2017, while sheep and beef numbers declined massively (MfE, 2019).

Worldwide, there have been high levels of agricultural intensification. For example, between 1961 and 1994, food production increased by 100% while arable land only increased by 10% worldwide (Tilman, 1999). New Zealand currently uses the land more intensively than in past decades, with more dairy cows per unit area than in previous decades (MfE, 2019). For instance, between 1994 and 2004 in New Zealand, there was an increase in nitrate use by 500% and a doubling of phosphate use when dairy farming productivity had an annual increase of 15% (MfE, 2006). Agriculture intensification requires greater use of fertilisers and pesticides to achieve more production and therefore causes increasing pollutants to waterways and lakes.

The agricultural development has certainly adversely affected water quality in lakes and other water bodies in New Zealand (Verburg et al., 2010). Lakes and waterways in farming areas have been polluted by excessive nutrients, sediment, trace metals and pathogens, affecting the ability of the water environment to support aquatic life and making it unfit for human uses such as recreation, cultural and aesthetic use, water supply and aquaculture (MfE, 2019). In 1993, the National Institute for Water and Atmospheric Research (NIWA) conducted a freshwater quality assessment in New Zealand and found that most freshwater bodies in agriculture-dominated catchments were in a poor state, reflecting agriculture-derived pollution in isolation or in addition to industrial or urban pollution (MfE, 2017; C. M. Smith, 1993). The major pollutants identified included pathogens, dissolved nitrogen, and dissolved reactive phosphorus and trace element sediments.

Another report compiled by NIWA in 2010 that tracked water quality trends in 112 lakes in New Zealand from 1990 to 2009, showed that 44% of the lakes were eutrophic or worse; 17% of the lakes deteriorated between 2000 and 2005, increasing to 28% between 2005 and 2009 when dairy farming was expanded to replace natural vegetation and riparian plants with grazing land (Verburg et al., 2010).

2.2 Farming History in New Zealand

Understanding the history of human settlement in an area and its associated land use change is vital in differentiating human impacts on a lake's condition from the natural conditions that existed before human arrival. In New Zealand, there are at least four major events related to land use changes that could have a bearing on lake sediment geochemistry and quality (Table 2.1).

Table 2-1 Notable history events affect land use change in New Zealand (John, 2006a; John, 2006b).

PERIOD	EVENTS	LAND USE ACTIVITIES
1300	Arrival of Māori	Localised deforestation, hunting and burning bush to support subsistence farming
1820 to 1840	Arrival of Europeans	Deforestation and farming on larger scale. Introduction of exotic grasses and trees.
1960s	Agriculture intensification	Farmland expansion,more intensive use of fertilisers and pesticides.
From 1990s	Increase in dairy farming (land conversion)	A step-change increase in converting farms to dairy operations, requiring more fertiliser, and increasing effluent generation.

Firstly, the settlement of Māori/Polynesian settlers in AD 1300 is associated with local land use changes such as deforestation and subsistence farming of crops such as sweet potato (kūmara) (Wilson. John, 2006b; McIntyre, 2002). Secondly, the arrival of Europeans in around AD 1820, saw the establishment of relatively large commercial farms and deforestation taking place at a larger scale (Wilson. John, 2006b; McFadgen, 2003). The Europeans established farms for crops such as wheat and livestock such as sheep and beef in different regions based on the weather and natural conditions of the regions. For instance, in the 1880s, Canterbury became known as an iconic sheep and wheat farming region (Wilson. John, 2006). Thirdly, more recently, agricultural intensification took place in the 1960s, when existing farms expanded through increased mechanisation and the use of fertilisers and chemicals to achieve more yield per unit area (McGlone & Wilmshurst, 1999). Finally, land use change in the South Island regions from the 1990s included a great increase in dairy farming, due to better irrigation and movement of North Island dairy farmers, who followed cheap land prices and long milking periods to the South Island (Amber, 2006; David, 2008; Wilson. John, 2006a). This period is associated with land conversion by many farmers from sheep and beef farming to dairy farming. In Canterbury, dairy cows increased by more than 100% (from 397,533 to 855,942 cows) between 2000 and 2012, while in Southland dairy cow numbers increased more than ten times (from 50,000 to 670,000 cows) between 1992 and 2012 (David, 2008; Wilson. John, 2006a). The increase in dairy farming has affected water quality because dairy farming generates more wastes than other livestock farming systems (Cichota & Snow, 2009).

2.3 Agricultural Sources of Trace Elements

Trace elements occur naturally at low concentrations that are tolerated by most organisms, and some can play an important role in metabolic processes in plants, humans and other animals (Reddy et al., 2016). However, higher concentrations of trace elements can become poisonous and toxic to plants and animals and pose health hazards to human beings. Some trace elements such as mercury and cadmium pose health hazards to humans because they accumulate in biotic systems, increasing in different levels of food chains (Alkarkhi et al., 2008; Bolan et al., 2004). In aquatic environments, high concentrations of trace elements accumulate in many organisms, damage their tissues and suppress growth (Bolan & Thiagarajan, 2001).

High concentrations of trace elements may occur naturally in an environment but they are mainly caused by anthropogenic activities (Bolan et al., 2004; Martin et al., 2017; Rainbow, 2018; Ward, 1990), such as mining, industrial activity, urban development, atmospheric deposition and agricultural development. When compared with others, agricultural activities are often considered to be less significant sources of trace elements (Frignani & Bellucci, 2004; Quinton & Catt, 2007), and they have been traditionally neglected in many risk assessments and research. However, long-term environmental problems as a result of trace element accumulation from agricultural areas have been observed to increase in recent years (Afzal et al., 2019; Du Laing et al., 2008; Zheng et al., 2008).

Studies of trace elements in sediments can show long-term impacts of anthropogenic activities and help in assessing associated risks (Zheng et al., 2008). Sediments, along with bound trace elements are transported within a catchment via wind, surface runoff and groundwater to contaminate waterways and lakes. In lakes, trace elements can be found in a dissolved state or attached to suspended and deposited sediments, depending on the trace element, as well as on chemical and physiochemical factors such as conductivity, pH, organic matter or salinity (Praveena et al., 2008). The trace elements that do deposit in sediment year by year can be detected in the columns of sediment cores. The quantities of trace elements found at various layers in the sediment cores can therefore be used to assess the level of pollution occurring through time in the catchment.

Trace elements are mainly applied to agricultural land through their presence in fertilisers and pesticides or as agricultural pharmaceuticals. The following section describes some of the trace elements that are commonly used in a New Zealand agricultural setting.

2.3.1 Cadmium (Cd)

Cadmium (Cd) is a trace element that has no biological function in plants and animals and is regarded as toxic to animals and humans even in low concentrations (B. J. Alloway, 1990; Lepp, 1995). When cadmium is ingested by animals or humans, it accumulates in the liver or kidney and can only be excreted in low quantities (Life Systems, 1989). Ultimately, this accumulation denatures body tissues in the organisms. Accumulation of cadmium in human beings has been reported to cause problems such as renal dysfunction, blood and liver problems, bone degeneration and cancer (ATSDR, 2014; Chaney et al., 1999).

According to Loganathan et al. (2003), there are mainly four sources of cadmium in rural areas or agricultural settings. Firstly, cadmium can be found in agricultural soils in areas where parent rock material includes igneous rocks and sedimentary rocks that contain cadmium (Adriano, 1986). The other three sources are related to anthropogenic activities: phosphorus fertilizers, atmospheric deposition from industries, and sewage sludge and industrial waste application to agricultural land.

In New Zealand, the major source of cadmium in agricultural settings is phosphate fertilisers, which are applied mainly for growing legume pasture (Loganathan et al., 2003). Cadmium first became an issue of concern in New Zealand in the 1980s when there were reports of high concentrations of cadmium in offal production from grazing animals. About 25% of tested sheep during 1988 to 1992 had cadmium concentrations above the maximum permissible concentrations (MPC) of 1 mg/kg fresh weight, a benchmark set by the New Zealand

Ministry of Health (1984)(Marshall, 1993). This was a major issue because it could create a tariff barrier for exporting sheep meat to other countries and tarnish the image of New Zealand as a country that produced safe food.

2.3.2 Arsenic (As)

Arsenic is a trace element that exists naturally as discrete deposits in the earth's crust, usually in powdery amorphous and crystalline forms. The element is of high concern worldwide because of its impacts on the environment and human health. High concentrations of arsenic can accumulate in plants, which are the basis of all food chains (Reay, 1972; D. G. Smith & Williamson, 1986). Animals and humans can be affected by consuming plants such as mint or watercress (Reay, 1972), and by drinking water with high concentration of arsenic (Smedley & Kinniburgh, 2002).

Arsenic can enter an environment naturally or through anthropogenic activities. Arsenic is ubiquitous in geothermal areas and volcanic zones such as Taupo volcanic zone (Aggett & Kriegman, 1988). Taupo volcanic zone is an area in the central North Island of New Zealand between Mt Ruapehu and White Island, in which waterways have natural arsenic levels higher than 0.01 mg/kg, the upper limit recommended for drinking water by the World Health Organization (WHO). Arsenic also occurs naturally in some groundwater. This can cause higher arsenic concentrations in agricultural soils when this type of water is used for irrigation (Gillispie et al., 2015).

Anthropogenic activities that contribute to higher concentration of arsenic include timber treatment, effluent discharge and the use of arsenic-bearing agricultural herbicides and pesticides. Arsenic-bearing copper-chrome-arsenate (CCA) is used as a preservative in timber treatment plants and is regarded as a major source of arsenic in terrestrial and aquatic environments (Bolan & Thiagarajan, 2001). Several studies have also shown that arsenic can leach out of the treated timber into surrounding soils (Chirenje et al., 2003; Stilwell & Graetz, 2001; Zagury et al., 2003).

In agricultural areas, arsenic has previously been used in several herbicides and pesticides. Historically, pesticides have been extensively used in horticultural farming; pesticides such as lead arsenate "($PbAsO_4$), calcium arsenate ($CaAsO_4$), magnesium arsenate ($MgAsO_4$), zinc arsenate ($ZnAsO_4$), zinc arsenite [$Zn(AsO_2)_2$] and Paris Green [$Cu(CH_3COO)_2.3Cu(AsO_2)_2$]" have been reported to contribute to increased concentrations of arsenic in soils (Merry et al., 1983; Newton et al., 2006); C. C. Tanner and Clayton (1990) also reported that the use of sodium arsenite ($NaAsO_2$) to control aquatic weeds has caused an increase in arsenic concentrations in some New Zealand waterways.

Arsenic has also been used in dips for sheep and cattle, as a pesticide to control fleas, lice and ticks (G. McBride et al., 1998; McLaren et al., 1998). McLaren et al. (1998) showed that more than 20, 000 sites in New Zealand were affected by this use of arsenic to control parasites.

2.3.3 Copper (Cu)

Copper is the third-most used trace element in the world after iron and aluminium. It is an essential trace element in the biological functions of both animals and plants (Brian J. Alloway, 2013). In plants, copper is essential in activating some enzymes during photosynthesis, disease resistance, seed production and water regulation (Rehman et al., 2019). In humans, copper is essential for production of blood haemoglobin, and helps in the maintenance of bones, blood vessels and the immune system. However, high concentrations are toxic to plants and animals and lead to problems in humans such as anaemia, damage to the kidneys or liver, stomach irritation and nausea (B. J. Alloway, 1990). Copper is also toxic to many aquatic organisms, even in low concentrations.

The major sources of copper that increase its flux through an environment include metallurgical, industrial and mining waste and urban storm water. Copper sources in urban environments include house roofs, water pipes, car brake pads and other copper-bearing materials that increase the amount of copper in the municipal stormwater and sewage sludge (Boller & Steiner, 2002). When these sewage sludge and industrial wastewaters are applied to, or irrigated onto, agricultural fields, they increase the amount of copper in the soils (Al-Khashman, 2009; Chen et al., 2005; Cheng et al., 2014).

Other sources of copper in agricultural fields include the use of fungicides, herbicides, pesticides, bio-solids and manure. Copper has been used as a fungicide (a mixture of lime, copper sulphate, and water) for grapes since the 1880s. Manure from pigs has also been reported to contain higher concentrations of copper than manure from cows and sheep (Nicholson et al., 1999; Xiong et al., 2010), because copper sulphate is added to pigs feed to inhibit bacterial activities in the stomach and maximise the use of the feed by pigs.

2.3.4 Zinc (Zn)

Zinc is an essential trace element to both plant and animal biological functions, so its deficiency leads to failure of these functions. In plants, zinc is essential in protein metabolism, carbonate metabolism (i.e., conversion of sugars to starch and photosynthesis), pollen formation and for providing resistance to fungal diseases (Brian J. Alloway, 2013; Kiekens, 1995). In the human body, zinc has been found to be essential in processes such as homeostasis, apoptosis, and immune responses and for those processes resisting the effects of oxidative stress, aging and diseases that come with age (Plum et al., 2010; Prasad, 2001; Stefanidou et al., 2006). In animals, zinc helps to activate enzymes that are relevant in processes such as protein synthesis, nucleic acid metabolism and carbohydrate metabolism (Prasad, 2001).

Nevertheless, high concentrations of zinc pose health problems and are toxic to both plants and animals. Elevated zinc causes anaemia and cholesterol problems in humans, and can lead to nausea and vomiting in children (Chattopadhyaya et al., 2014). In an aquatic environment, higher concentrations of zinc in aquatic organisms may eventually affect the entire food chain(Broadley et al., 2007; Whitton et al., 1982). In plants, high zinc concentrations (between 100 to 500 mg/kg) causes phytotoxicity (Kabata-Pendias, 2001; Mozhdeh et al., 2019). As a result, plants have stunted growth and reduced chlorophyll production (Chaney et al., 1999; Kabata-Pendias, 2001).

Zinc is naturally available in the Earth's crust, but its availability is increased in the environment by anthropogenic activities. Natural background concentrations of zinc in the Earth's crust are estimated to be between 70 and 80 mg/kg (Chaney et al., 1999; Kabata-Pendias, 2001). Concentrations of zinc in magmatic rocks have a wide range distribution (Kabata-Pendias, 2001), while sedimentary rocks such as limestone, dolomites and sandstones have concentrations in the range of 10 to 30 mg/kg, whereas organic-rich sedimentary rocks such as shales may have 80 to 120 mg/kg of zinc (Kiekens, 1995).

Higher concentrations of zinc are mainly caused by anthropogenic activities such as atmospheric deposition from industries, galvanising, car tyre rubber and car exhaust fumes (Berthelsen et al., 1995; Councell et al., 2004; Gunawardena et al., 2013). In agricultural areas, zinc can be elevated in both pastoral and horticultural farming areas. In pastoral soils, zinc is present in agrochemicals such as superphosphate fertilisers, pesticides and lime amendments (Brian J. Alloway, 2013; Kabata-Pendias, 2001). Zinc is used to dose ruminant animals, to prevent the *mycotoxic* ruminant disease *pithomycotoxicosis*, more commonly known as facial eczema. Several studies have emphasised the increased use of facial eczema remedies over the past decade as the main source of zinc in pastoral soils (LMF, 2009; M. D. Taylor, 2011). In horticultural soils, the common source of zinc is the dithiocarbamate fungicide which is sprayed in chelated form (Kanemoto-Kataoka et al., 2018).

2.4 Lake Sediments

Understanding the effects of past human land use activities is key in evaluating their current and future impacts on the environment (Swetnam et al., 1999). Natural archives, along with historic documents such as early maps or recorded events, can be used to investigate the impacts of past land use activities (Ramlal et al., 2003; Vitousek et al., 1997). Lake sediments are one such natural archive, and can provide a record of past land use changes (Smol, 2002); both natural environmental changes and changes induced by anthropogenic activities in a catchment. They can be used to identify the pristine conditions, and to differentiate naturally induced changes from those induced by man, as sediments are less dynamic than water or biota indicators and can provide a long-term record.

A variety of physical and biogeochemical processes lead to the formation of lake sediment pile (Cohen, 2003). Suspended particles in the water column reflect different environmental conditions in the lake catchment area, such as deforestation, land use change, floods and erosion. They also reflect the environmental conditions within the lake, such as eutrophication, chemical precipitation and aquatic biodiversity. Suspended particles are therefore a mixture of inorganic (mineral) and organic (biotic) materials, and settle with time, depositing in regular laminated couplet varves as shown in Figure 2-1 below (Lotter et al., 1992). Regular laminated couplet varves represent annual duration, and can show seasonal variations along the sediment core (Beer & Sturm, 1995).

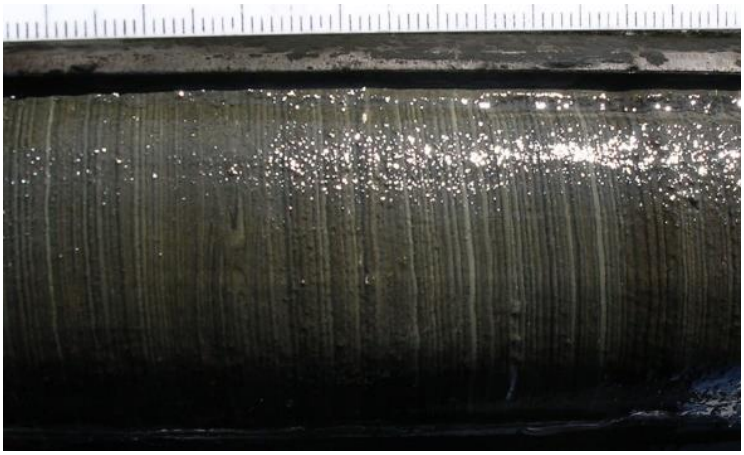

Figure 2-1 Laminated varves of lake sediment cores (Saarinen (2010))

According to Beer and Sturm (1995), the study of sediments using biological, chemical, mineralogical and paleomagnetic methods can help to extract some important information such as:

- global or local climate based on isotope stability and pollen analyses information;
- anthropogenic activities in the catchment such as agriculture, deforestation, urbanisation, eutrophication, pollution by trace elements and organic materials;
- atmospheric deposits both natural and pollution from industry emissions; and
- natural extreme events such as earthquakes, floods and volcanoes.

2.4.1 Sediment dating

The relevance of any archive is dependent on how datable it is. The long-term timeline in a sediment record can be seriously disrupted by factors such as bioturbation, remobilisation of chemicals, slumps and natural catastrophes (Beer & Sturm, 1995) however, there are several methods that can be used to date lake sediments. The most precise methods are those that count the individual annual couplets (varves). A good example for these methods is the luminescence dating method (Buylaert et al., 2012; Lian & Roberts, 2006). Other methods use radioactive decay and absolute time markers. The most popular radioactive decay methods are ^{210}Pb and ^{14}C (Hajdas et al., 1995; von Gunten & Moser, 1993). The absolute time markers in dating methods include volcanic ash layers and ^{137}Cs horizons from 1963 (related to nuclear weapon testing) or from 1986 (the Chernobyl accident). Well-recorded natural events such as floods and earthquakes are also used as absolute dating methods. To interpret the time scale, sediment records are analysed for absolute time markers and correlated with records of diatoms/pollen stratigraphy, magnetic vulnerability and geochemical parameters such as trace elements and nutrients (Beer & Sturm, 1995).

Globally, there are several studies that have used lake sediments to study the record of past human influences on lakes. Trace elements have been used as indicators of human-induced or natural changes or changing atmospheric deposition in a catchment (Bing et al., 2013; Norton & Kahl, 1991; Wolfe & Härtling, 1997). Carbonate minerals have been used as indicators of climate or trophic change (Westphal et al., 2010). Several

studies have presented changes in stable isotopes as indicators of changes in climate, salinity, or trophic state (Dawson et al., 2007; Koinig et al., 2003; Schmidt et al., 2002; Smol & Cumming, 2000).

There are several international studies that have studied the accumulation of trace elements in lake sediment cores, to assess both urban and rural pollution (Acevedo-Figueroa et al., 2006; Bing et al., 2013; Ekoa Bessa et al., 2018; Ioannides et al., 2015; Lin et al., 2008; Merry et al., 1983; Qi et al., 2010; Zahra et al., 2014). However none of these studies have had a special concentration on pollution from rural land uses only, nor studied long term impacts in a setting just like New Zealand which has experienced land occupation of both the native and Europeans.

2.4.2 Previous studies of New Zealand lake sediments

Several studies have used lake sediments to reconstruct past human and natural changes in New Zealand. Reid et al. (2004) and Woodward and Shulmeister (2005) worked on Lake Forsyth, Pugh and Shulmeister (2010) on Lake Heron, Augustinus et al. (2006) on Lake Pupuke, Irwin (1972) on Lake Pukaki, Irwin (1971) on Lake Manapouri, Irwin (1978) on Lake Tekapo and Lake Ohau, and Pickrill and Irwin (1983) on Lake Tekapo.

A few other researchers specifically concentrated on the limnology and chemistry of lake sediment cores in New Zealand. Glasby (1975) studied the geochemistry of superficial lake sediments of lake Tekapo, and Chittenden et al. (1976) studied the chemistry and mineralogy of the sediment cores of Lake Rotoroa and Lake Rotoiti. Stoffers et al. (1983) conducted a reconnaissance survey of the mineralogy and geochemistry of some New Zealand lakes and the nearshore sediments. They conducted geochemical analysis of sediment cores from four different environments: South Island glacial lakes, South Islands fiords and sounds, North Island volcanic lakes and North Island harbours and estuaries. Their results showed that the principal differences in sediment geochemistry among the lakes studied was generally associated with the lithology of the sediments and productivity of the lake waters. They recommended their results be used as background information for future studies on sediment geochemistry of the lakes in New Zealand.

Koyama et al. (1989) also studied the “mineralogy and geochemistry of sediments from Lakes Taupo and Waikaremoana, New Zealand”. Their main focus was also to provide baseline concentrations of trace elements in lakes that were relatively uninfluenced by anthropogenic activities.

Most of these studies provided important information on the baseline concentrations of trace elements in New Zealand lakes; however, they were done some decades ago. There was a need, therefore, to conduct this study to specifically assess trace elements as indicators of more recent agricultural rural land use change in New Zealand.

Chapter 3

Methodology

3.1 Study Areas

Six New Zealand lakes with catchments that have varying records of agricultural intensification and transformation were selected for this research. The lakes were Lake Pearson, Lake Forsyth (Te Roto o Wairewa), Lake Heron, Lake Ngāpouri (Opouri), Lake Tutaeinanga and Lake Moawhitu. The proposed lakes include both lowland/coastal lakes with a very long history of agricultural intensification, and high-country lakes that have undergone more recent agricultural intensification.

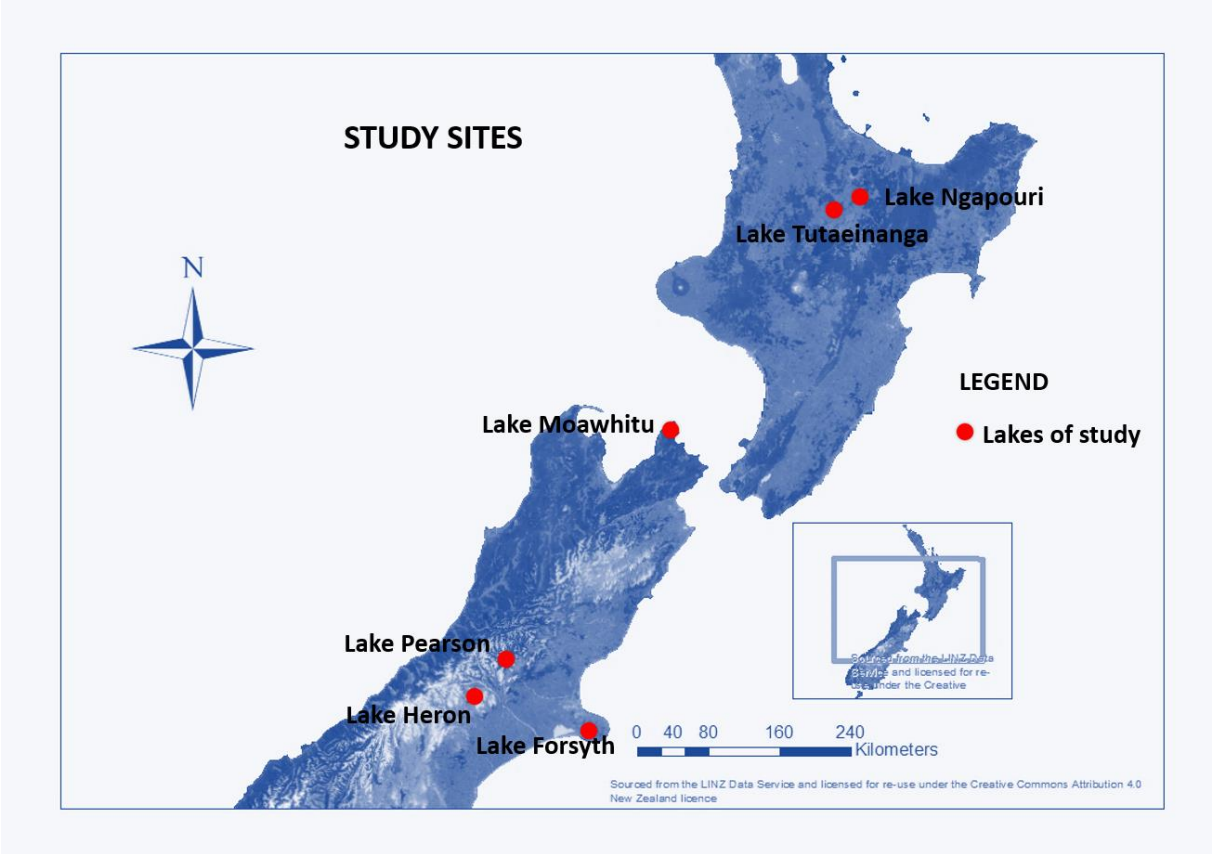

Figure 3-1 Map of New Zealand showing the selected study lake locations (Map created by the author using ArcGIS software and using New Zealand lakes shape file present in Lincoln university GIS database)

The selection of the study lakes for this project was determined by two main factors.

- They have catchments that have long-term histories of being predominantly used for agriculture. This was established by studying Google Earth images and reviewing literature on each lake.

- They were ranked as priority lakes under the Lakes380 project. The Lakes380 project ranked the lakes according to their preliminary findings. Priority lakes had to have adequate sedimentation to show impacts of human-induced land use changes for the previous 1000 years. The six lakes were determined

in a meeting with the scientists from GNS and Cawthron Institute working with the Lakes380 programme.

3.1.1 Lake Forsyth/Wairewa

Lake Forsyth (Te Roto o Wairewa) is a shallow lake (<4m deep), located in the southern part of Banks Peninsula in the Canterbury region of the South Island, New Zealand. It has a maximum surface area of 6.276 km² with a maximum length of 7.6 km and a maximum width of 1 km. The lake has a catchment area of about 110 km^2, which is mostly steep hilly country areas used for pastoral agriculture. The lake receives most of its inflows from the Okuti and Okana Rivers, which join just before the lake to form the Takiritawai River. Other inflows come from groundwater and small streams and runoff that goes directly into the lake.

Figure 3-2 Aerial view of Lake Forsyth/Wairewa looking towards the coast (S. A. Waters, 2016)

The eastern end of the lake is separated from the Pacific Ocean by a narrow gravel barrier (<100m wide) known as Kaitorete Spit. Kaitorete Spit is a relict spit and an active-barrier beach complex which has evolved over a period of 8000 years as an accumulation of materials transported north along the coast of Canterbury Bight by long sea currents (J. M. Soons et al., 1997; Woodward & Shulmeister, 2005). The barrier is artificially opened occasionally to reduce flooding of roads, farmland and surrounding residential houses. The first artificial opening occurred in 1866, and currently it is opened one to three times every year depending on the rainfall (Reid et al., 2004; Jane M. Soons, 1998; Woodward & Shulmeister, 2005). Even though the intermittent opening to the sea has the advantage of controlling floods and flushing sediments and nutrients, it affects the biodiversity of the lake. “The intermittent opening limits biodiversity by restricting the fauna and flora that inhabit the lake to those taxa that tolerate significant salinity variations” (Schallenberg & Schallenberg, 2013).

History of human occupation in the catchment

According to Wilson. John (2006b), the first Māori who settled in the Canterbury region about 600 to 700 years ago, mainly lived near the coast (beside productive wetlands) and around Lake Forsyth (Te Roto o Wairewa) and Lake Ellesmere (Te Waihora). Banks Peninsula was generally preferred to inland areas because it provided resources from both the sea and the forest (Wilson. John, 2006b). The presence of Māori in Banks Peninsula is associated with the initiation of forest clearing and led to some changes in the land cover and slope stability (McIntyre, 2007).

The first recorded landing of Europeans in the Canterbury region was in 1815 or 1816 when a sealing ship docked at Akaroa to trade flax and potatoes (Wilson. John, 2006b). The organised settlement of the Europeans in the area was opened after the signing of the Treaty of Waitangi in 1840. The French and Germans settled in Akaroa in August 1840, while British settlers established farms in the Canterbury plains. The developments in the Lake Forsyth catchment were delayed until 1895 and until then the land was covered in broadleaf/podocarp forest. The development led to the removal of trees for timber or by burning, either accidentally or deliberately, to create areas for pastoral agriculture (Petrie, 1963). By 1907, the lake had already become prone to recurring blooms of the hepatotoxic cyanobacteria *Nodularia spumigena Mertens*, which led to the death of large numbers of fish and other aquatic life (Elliott, 2002; Eric, 1992).

According to the study by Woodward and Shulmeister (2005), deforestation in the Lake Forsyth catchment increased freshwater overland flow that entered into the lake, causing salinity fluctuations and bringing more nutrients into the lake system. Deforestation also increased soil erosion in the catchment and consequent sediment accumulation in the lake (Reid et al., 2004; Woodward & Shulmeister, 2005). The sediment accumulation rate for the lake was 0.88 mm/year before 1840 (pre-European) and increased almost 4-fold to 3.7 mm/year after the European land use activities (Woodward & Shulmeister, 2005).

According to the report by Miller and Webster-Brown (2013) the major sources of sediments over the summer are from the Okuti and Okana Rivers and there was little or no input of sediments in the lake from other tributaries or surface runoff in the absence of heavy rainfall over the summer period.

The current water quality of Lake Forsyth is generally described as turbid and hypertrophic and it experiences regular toxic blooms of cyanobacteria, mostly *Nodularia spumigens* and less commonly *Anabaena spp.* (Schallenberg & Schallenberg, 2013). The current water quality monitoring programme for Lake Forsyth from 2002 also showed that the water in the lake has consistently been very poor with trophic level indicators (TLI) ranging between 5 and 8.5 (supertrophic) (LAWA, 2017a). The poor water quality has an impact on the biodiversity of the lake (Jellyman, 2007; Reid et al., 2004; Woodward & Shulmeister, 2005). The lake has historically been a source of food (mahinga kai) for Ngāi Tahu (the indigenous Māori people in the South Island) and it is currently their only customary lake in the South Island. Te Wairewa Rūnanga, one of the 18 Ngāi Tahu Rūnanga, are the custodians or kaitiaki of the Lake Forsyth. Te Wairewa Rūnanga recognized the restoration of Lake Forsyth in the area as priority.

3.1.2 Lake Pearson

Lake Pearson (43.1014° S, 171.7742° E) is a high-country lake of glacial and fluvio-glacial origin in the Cass district, in the upper part of the Waimakariri River in the Canterbury region of the South Island. The lake is adjacent to State Highway 73 and it is 32 km south-east of Arthur's Pass and 56 km north-west of Sheffield in central Canterbury. It is a relatively small lake with an area of 202 hectares and a maximum depth of 17 metres.

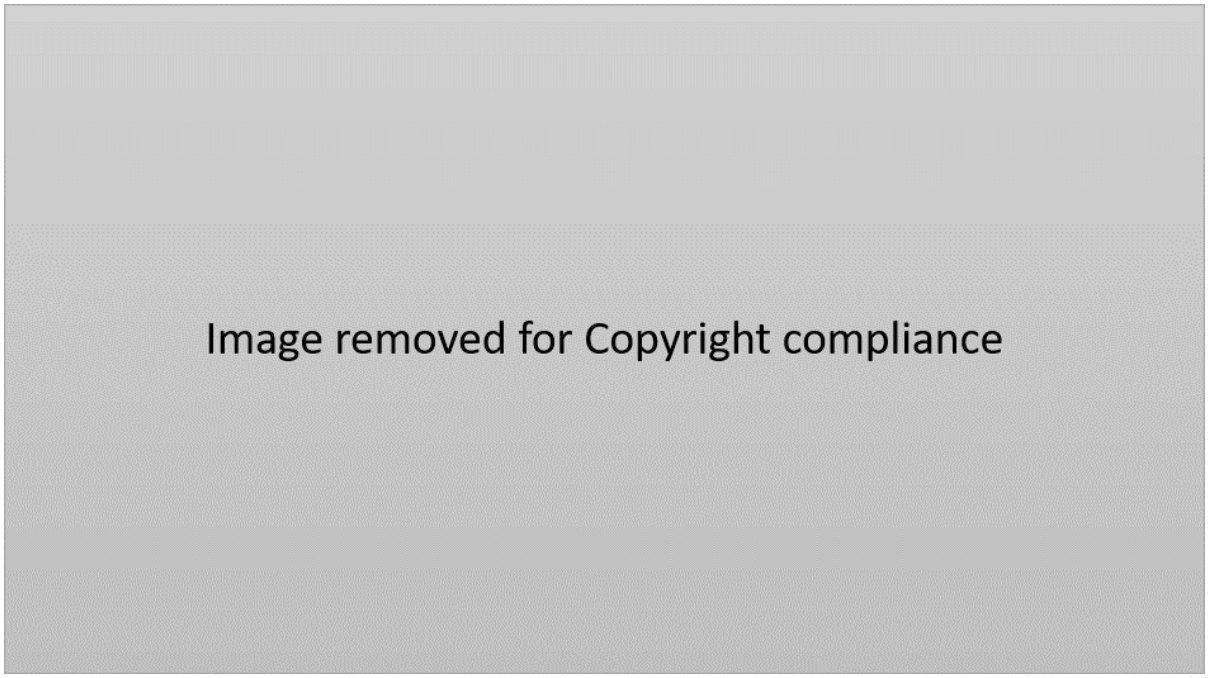

Figure 3-3 Side view of Lake Pearson (Fishingmag, 2015)

Lake Pearson has several values including recreation and tourist activities such as game-bird hunting, boating and camping. The lake supports a large population of the threatened aquatic fern *Pilularia novae-zelandiae* and it is regarded as the most important habitat in the Cass district for an endangered species of Crested Grebe (Podiceps cristatus australis) in New Zealand.

Human occupation

Pre-European historical evidence, such as rock drawings, charred moa bones and the charcoal of forest fires, show the presence of early Polynesian hunters in the Castle Hill basin about 400 to 800 years ago (McLeod & Burrows, 1977). The burning of large tracts of beech forest around Cass are associated with these early hunters. These fires were made to aid hunting or to create passage through thick forested areas, and they caused the local destruction of beech forest and reduction of the tall tussock grassland above the treeline (Molloy, 1977). The destruction of the vegetation by the fires exposed the soil to wind, water erosion and ice penetration.

Pre-European history also records that the early Polynesians used the pass, now called Arthurs Pass as a route to the West Coast, where they collected supplies of pounamu, also known as greenstone (McLeod & Burrows, 1977).

According to McLeod and Burrows (1977), the first European settlers in the Waimakariri basin, J. Pearson and T. Sidebottom thoroughly explored the area around Cass in 1857, after the more accessible tussock grasslands of the Canterbury Plains had been occupied by the first European settlers in the region. J. Pearson had been commissioned by a group of sheep graziers, immigrants from Australia, to find sheep country. These explorers burnt the vegetation, especially scrub and grassland, and some forest (Molloy, 1977). By the end of 1858, homesteads had been established at Craigieburn and Grasmere by J. Hawdon, who took up Grasmere, Craigieburn and Riversdale as sheep runs.

The land around Lake Pearson has undergone different land tenure systems. Currently, Lake Pearson's bed and the surrounding iparian reserve strip around is owned by the Crown, available for public recreational use only and not for sale (Cromarty, 1996). Lands adjacent the lake are included within three Crown pastoral "runs" (large farm holdings) which are used for sheep, cattle and deer farming. Two of the runs have freehold (privately-owned) land on the valley floor bordering the northern and southern ends of the lake. Agriculture activities close to the lake are known to be the main contributors of the nutrients in the lake (Cromarty, 1996).

3.1.3 Lake Heron

Lake Heron is a high-country lake located between the Upper Rakaia and Ashburton Rivers in the Ashburton district, in the Canterbury region of the South Island of New Zealand. The lake is one of the Ashburton Lakes recreational area, which comprises a group of high-country lakes and walking tracks that provide for a wide range of recreational activities, surrounded by a spectacular Canterbury scenery.

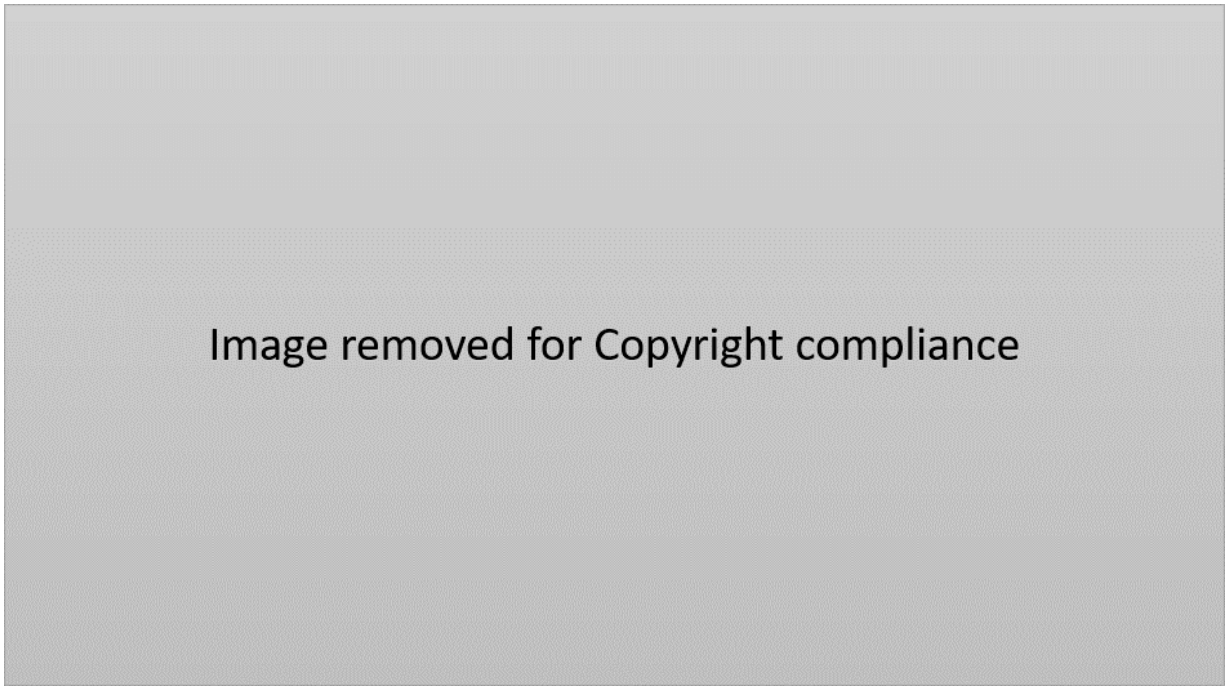

Figure 3-4 Lake Heron in the Ashburton Lakes district. (Google Maps, 2020a)

Lake Heron basin has been subjected to several historical studies because the area has experienced many glaciations. The basin is an inter-montane basin, 30 km long and 7–8 km wide, between the Arrowsmith Range to the west and the Mount Somers Range to the east. The basin resulted from reverse and back thrusting on

faults, that were formed between the Canterbury front ranges and the main ranges of the Southern Alps (Pettinga et al., 2001).

Human occupation in Lake Heron catchment

Several sites in the Rakaia catchment show the presence of Polynesian (Māori) people before the arrival of Europeans (McIntyre, 2007). Māori used what are now called Whitcombe and Browning Passes in the catchment to find access to West Coast. The movements of Māori in the area are associated with the burning of vegetation which led to extensive modification of the land cover and triggered a phase of slope instability and soil erosion (Burrows, 1977).

The Canterbury Association was formed by European settlers in 1848 to facilitate the development of Banks Peninsula and the plain areas between the Ashburton and Waipara Rivers. Due to high land prices, the applications and development of the hilly country were delayed until 1852 (McIntyre, 2007). The development of the south part of the Rakaia River was further delayed due to transport and communication problems caused by the river. At the time of occupation of Europeans, tussock and matagouri (*Discaria toumatou)*, interspersed with wild spaniard *(Astelia sp.*), dominated vegetation in the upper Ashburton region. The first 5 to 10 years of the European settlement is associated with the burning of tussock and scrubland to encourage young growth to be palatable to stock (McIntyre, 2007). The burning also modified the land cover and triggered slope instability.

Lake Heron has an *average* water quality and a *moderate* ecological healthy status (LAWA,2017a). The water quality has changed from having *excellent* conditions before 2003 to *average* water quality in 2018. The change in water quality is attributed to the farming intensification around the catchment (LAWA, 2017b).

3.1.4 Lake Ngāpouri and Lake Tutaeinanga

Lake Ngāpouri (19 ha) and Lake Tutaeinanga (3 ha) are both located in the Waikite Valley, west of the Waiotapu Thermal Area, in the Waikato Region, North Island, New Zealand. Lake Tutaeinanga and Lake Ngāpouri are feeds into Opōuri Stream and the Waiotapu River which eventually feeds eventually the Waikato River. The catchments for both lakes are fully covered by dairy and sheep farms.

Figure 3-5 Lake Tutaeinanga and Lake Ngāpouri in the Waikato region and Bay of Plenty region – (Google Maps, 2020b).

Human Occupation

History accounts show that the Waikato is the ancestral region of several Māori iwi (tribes) that arrived in New Zealand by canoe in AD 1300 (Swarbrick, 2015). The tribes include Ngāti Maniapoto, Ngāti Toarangatira (Ngāti Toa), Ngāti Raukawa, tribes of the Marutūahu confederation, Ngāti Mahuta and Ngāti Hauā. They settled throughout the region, especially on hilltops, beside lakes or harbours where they could fish or hunt.

The first Europeans arrived in the Waikato region as traders and adventures in the 1820s and as missionaries in the 1830s (Swarbrick, 2015). The missionaries established schools and churches and they also taught farming techniques to the Māori tribes. The Māori farmers in Waikato were able to produce different farm products and sell them in Auckland, Australia and the United States of America (USA).

The first European settlers were soldiers who were later followed by farmers who established large farms and estates. Most of the native forests in the region were cleared for farming and some that remain are only found in forest parks and on mountain ranges (Swarbrick, 2015).

The Waikato region has ideal conditions for dairy cows, and dairy herds account for about 33% of the national herd (DairyNZ, 2019). The high rainfall, sunshine and mild winter temperatures make it possible to grow grass throughout the year. Other farming types include sheep and beef in high-country areas and horse breeding.

Dairy farming in the Waikato region has contributed to the degradation of freshwater quality in streams, rivers and lakes. According to a study in the Waikato region (Holz, 2004), streams in catchments that are covered by dairy farming have degraded water quality compared with streams in catchments that are covered by native forest.

Lake Ngāpouri and Lake Tutaeinanga are highly eutrophic and they experience frequent nuisance algal blooms, which are driven by high farm nutrients, such as nitrogen (N) and phosphorus (P), inputs from the catchment and high internal P loads released from sediments during summer stratification (Kusabs, 2017).

3.1.5 Lake Moawhitu

Lake Moawhitu is a small coastal lake located at the top of South Island in D'Urville Island (Rangitoto ki te Tonga) in the Marlborough region. The lake has an approximate surface area of 37 ha with an average depth of 8.1 m and a maximum depth of 13 m. Lake Moawhitu and the surrounding wetland complex is said to have been formed by the evolution of the coastal sand dune that formed a block to the river valley that was draining southward to Greville Harbour. The main inflow of the lake is a small stream at the north end of the lake and its outflow is a small culvert that drains through a wetland to the western end of the beach (Kelliher et al., 2017). Lake Moawhitu has a small catchment area of about 214 ha, mainly characterised by steep slopes (see Figure 3-6).

Human occupation

History accounts show that the first Polynesians settled in the catchment in AD 1300 and evidence of their presence has been found in the Marlborough region (McKinnon, 2016). Some remains of Māori adzes, made from argillite rock were found on D'Urville Island. History also shows that many Māori tribes from the North Island migrated to settle in Marlborough after the 1824 battle of Wairua. (McKinnon, 2016). During this period the Ngāti Koata tribe and a hapū (subtribe) of Ngāti Toa settled on D'Urville Island. Lake Moawhitu was also known as an important source of mahinga kai (food) mainly tuna (eel) for the Ngāti Koata (local iwi).

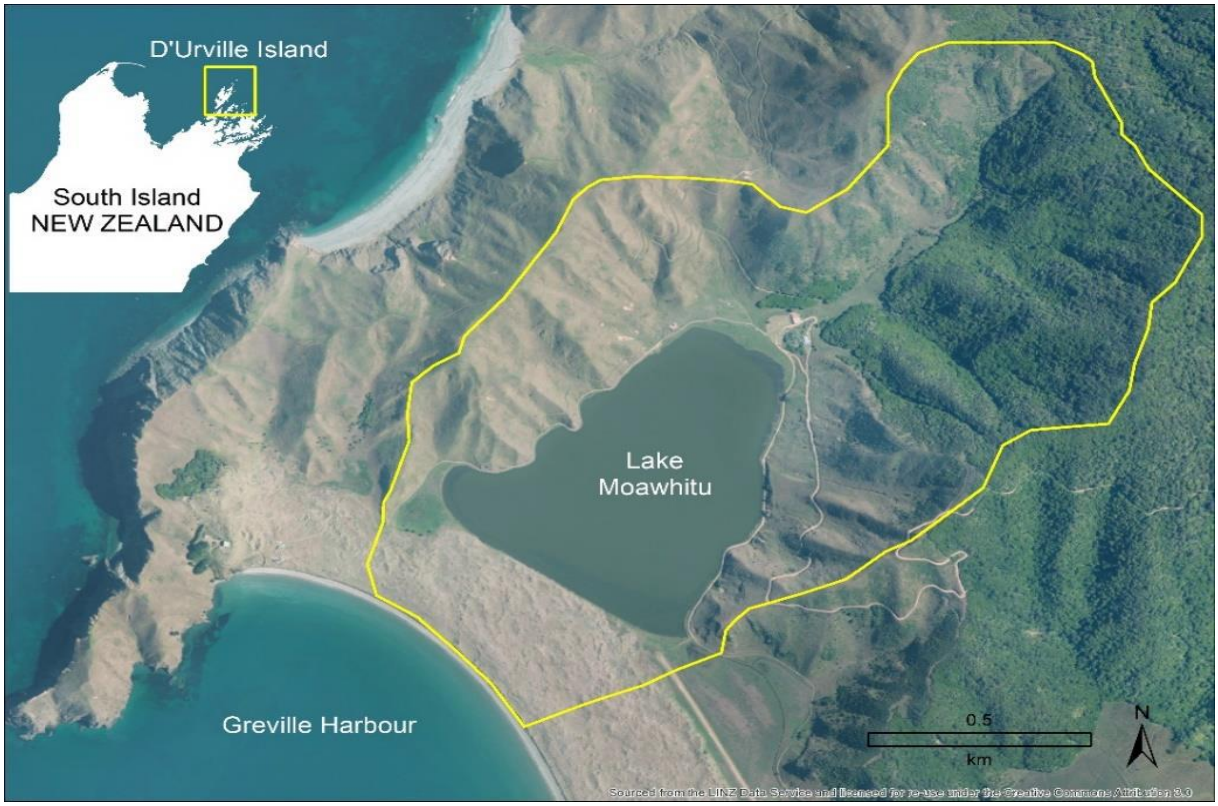

Figure 3-6 Aerial satellite map of Lake Moawhitu and its predicted catchment boundaries (Kelly et al., 2019)

Europeans arrived in the Marlborough region in the early 18th century (McKinnon, 2016). In 1843, there were fights over land ownership between the Europeans and Ngāti Toa. This led to the death of four Māori and twenty Pākehā (New Zealanders of European descent). The arrival of Europeans in the region led to the removal of native

vegetation and the establishment of large sheep farms and beef farms and vineyards. The catchment was covered by farms until 2004 when it was purchased by the Nature Heritage fund and passed to the Department of Conservation (DOC) (Kelliher et al., 2017). Currently the land is covered predominantly by high-producing exotic grassland (about 47.7%), low-producing grassland (9.4%), indigenous forest (17.6%), broadleaved indigenous hardwoods (7.8) and lake or wetland (17.5%). Currently the lake has high concentrations of nutrients and experiences frequent algal blooms, causing the Ministry for the Environment (MfE), DOC and Ngāti Koata to initiate a project to improve water quality and the ecological health of the lake.

3.1.6 General description of the geology and farm types in the lakes' catchments.

Farm types

Agriculture is one of the largest industries in New Zealand. The country is mainly characterised by pastoral farming of cattle and sheep, but horticulture is also common. The chosen lakes for this study were selected to cover several land types that are common in New Zealand: highland lakes that are associated with sheep and beef farm types, lowland lakes that are associated with mainly dairy and cropland farms and coastal lakes that are usually covered by many farm types. The types of farms determine the type and quantity of trace elements that are used at the farm and can be transported and deposited into lakes.

The catchments of the lakes studied in this research did not cover horticultural farms, mainly because at the time this study began, there were no plans by the Lakes380 project to core lakes near horticultural farms. Most of the catchments of the lakes studied are covered by sheep and cattle farms except in the catchment of Lake Forsyth which has many farm types. More details are shown in Table 3.1. The farm types were determined in Arc-GIS using shape files of Agribase 2014 for farm boundaries in Canterbury and Agribase2006 for national farm boundaries.

Table 3-1 Types of farms in the catchments of the six lakes studied, determined in Arc-GIS using shape files of Agribase 2014 for farm boundaries in Canterbury and Agribase2006 for national farm boundaries(Canterbury Maps, 2014) .

LAKE	FARM TYPES
Tutaeinanga	Pasture (dairy) A small patch of sheep and beef
Lake Ngāpouri	Pasture (dairy) Indigenous forest patch identified (<2ha).
Lake Forsyth	Sheep and beef (dominant) Dairy Beef Sheep Viticulture (about 5.4 ha only) Forestry Lifestyle blocks Grazing other people's stock Native bush (2040 ha)
Lake Pearson	Sheep and beef Sheep (dominant)
Lake Heron	Sheep and beef (dominant) Native forest

Lake Moawhitu	Was covered with beef farms (but now used for conservation purposes – since 2004)

Lithology

The knowledge of the general lithology of the catchment is important in differentiating the source of the trace elements in the sediment cores, as originating either from natural occurrence or from anthropogenic activities. The lithology of the catchments of the lakes in this study were determined by using the GIS layer of Land Resource Information System Spatial: Data Layers provided by Landcare Research New Zealand Ltd (Newsome et al., 2008). More details are in Table 3.2.

Table 3-2 Showing types of lithology of the catchments of the six lakes studied, based on Landcare Research database lithology (NZLRI Ed1) (Newsome et al., 2008), Land Resource Information System Spatial: Data Layers.

LAKE	Lithology	GENERAL DESCRIPTION
Tutaeinanga	Igneous (volcanic rocks)	Availability of ashes older than Taupo pumice Lavas, ignimbrite and other 'hard' volcanic rocks Unconsolidated to moderately consolidated clays, silts, sands, tephra and breccias Presence of Kaharoa and Taupo ashes
Lake Ngāpouri	Igneous (volcanic rocks)	Taupo and Kaharoa breccia and pumiceous alluvium Availability of ashes older than Taupo pumice Lavas, ignimbrite and other 'hard' volcanic rocks Unconsolidated to moderately consolidated clays, silts, sands, tephra and breccias Presence of Kaharoa and Taupo ashes
Lake Forsyth	Igneous (basaltic rocks)	The whole of Banks Peninsula is a 5-million year-old volcanic complex with varying lithology Presence of surficial rocks (loess and alluvium/colluvium and glacial drift)
Lake Pearson	Surficial rocks and strongly indurated sedimentary rocks	Alluvium/colluvium and glacial drift Greywacke
Lake Heron	Surficial rocks and strongly indurated Sedimentary rocks	Loess and alluvium/colluvium and glacial drift Greywacke
Lake Moawhitu	Igneous rocks	Ancient volcanoes, minor intrusive (dikes and sills)

3.2 Sediment coring and sampling

Figure 3-7 The Lakes380 team members (Sean Waters, Chris Moy, Reece Martin) and the author coring sediments at Lake Forsyth/Wairewa using a Uwitech gravity corer.

Sediment coring was done in collaboration with the Lakes380 project. The coring process involved using a 2-m-long Uwitech gravity corer (65 mm diameter) to retrieve sediment cores from the deepest part of the lake. The cores were chilled at 4 ^{o}C in complete darkness and transported for storage at GNS Gracefield, Lower Hutt in Wellington where subsampling took place. Four cores were taken per lake and one core was split down the middle. One half of this was subsampled, and the other half scanned using a hyperspectral scanner and an ITRAX XRF scanner at University of Otago. The remaining cores were stored by freezing them in total darkness for future analysis. The subsampled cores were later analysed for DNA, *chironomids,* carbon/nitrogen, pollen and diatoms by Lakes380 project scientists, for their various research studies, and for various geochemical markers by the author.

For the analysis of trace elements for this project, cores were subsampled in small 5cc tubes at an interval of 1 cm (about 1.2 g to 4.0 g per cm) and transported from the storage facility in Wellington to Lincoln University, in insulated boxes with ice packs, for digestion and analysis.

Sediment cores from Lake Forsyth, Lake Heron and Lake Pearson were cored in November 2019 within the timeframe of this research work, so the author was able to participate in the fieldwork. However, cores from Lake Moawhitu, Lake Ngāpouri and Lake Tutaeinanga were collected by the Lakes380 project team before the start of this research project. Cores from Lake Moawhitu were collected in September 2019, while cores from Lake Ngāpouri and Lake Tutaeinanga were collected in April 2019.

3.3 Geochemical analysis

This analysis involved determining trace element (Zn, Cu, Cd, As, Al, Pb, Fe and Mn) concentrations along the sediment core profile. The subsampling of the core for geochemical analysis was designed to target the period of agricultural change that occurred when Europeans arrived in New Zealand and started to establish large

commercial farms. The intervals for subsampling sediments for trace elements analysis were based on the chronology developed by the Lakes380 project, as detailed below.

3.3.1 Dating and pollen analysis

Given that it is very expensive to date sediments using radiometric methods, this research relied on pollen identification to establish a chronology of events. Dating using radiometric methods was being done by the Lakes380 project for some of the lakes in this study but the results were not available within the timeframe of this study. Pollen analysis focussed on the presence of exotic taxa such as sorrel (*Rumex*), willow (*Salix*) and pine (*Pinus*), as well as fern content, to indicate changes of vegetation that came after the arrival of Europeans. The presence of charcoal deeper in the sediment core was used to indicate the arrival and vegetation changes caused by Māori (Moore, 1970).

Pollen analysis was completed by the Lakes380 researchers at GNS laboratory in Wellington. Pollen extraction was carried out using standard laboratory techniques (10% hot KOH, 40% HF, and acetolysis) as described by Faegri et al. (1989) and included the addition of exotic Lycopodium tablets to permit the calculation of pollen concentrations. Pollen identifications were made with reference to standard texts (e.g., Pocknall, 1981a-c; Large & Braggins, 1991; Moar, 1993) and the New Zealand pollen reference collections held at GNS Science. For each sample, pollen taxon values were expressed as percentages of a minimum pollen sum of either 150 or 250 grains. This sum included pollen from all dryland plants excluding herbaceous swamp plants and ferns.

Table 3-3 Sediment depth (cm) corresponding to the European era, the Polynesian (Māori) era and prehuman conditions, based on the pollen analysis results.

LAKES	EUROPEAN ERA	POLYNESIAN (MĀORI) ERA	PREHUMAN ERA
Tutaeinanga	0–25.5	25.5–55.5	Below 55.5
Ngāpouri	0–38.0	38.0–64.0	Below 64.0
Forsyth /Wairewa	0–30.0	30.0–54.0	Below 54.0
Heron	0–22.0	22.0–91.0	Below 91.0
Pearson	0–18.0	18.0–26.0	Below 26.0
Moawhitu	0–34.5	34.5–66.5	Below 66.5

The core for Lake Tutaeinanga could not continue beyond the depth of 57 cm because of the dense thick volcanic ash at this depth, which may be associated to the Kaharoa volcanic eruption that occurred around AD 1314 at Mount Tarawera (Hogg et al., 2012). For Lake Heron, only the sediment core of 91 cm was collected and was simply not deep enough to collect prehuman era sediment.

3.3.2 Subsampling layout

Since the main emphasis for this study was on the land-use changes occurring after the arrival of the Europeans, the subsampling interval for the European era was at 3 cm, while for the Polynesian and prehuman era was at

6 cm. For Lake Tutaeinanga, however, subsamples were at 1 cm intervals in the European era and at 3 cm intervals in the Māori era, as they were subsampled before a well-established methodology for this study had been developed. Figure 3-5 shows the depth intervals in centimetres at which subsamples were taken for geochemical analysis for each lake.

3.3.1 Sediment digestion

The subsamples were digested and prepared for inductively coupled plasma – optical emission spectrometry (ICP-OES) analysis, at Lincoln University's Waterways Centre Water Quality Laboratory. The subsamples, taken at 3 or 6 cm intervals, were dried at 40 °C for at least 24 hours and then ground and sieved through a 67-micron sieve. A 100 mg sample of sediment ($M_{sediment}$) from each sample was digested in 10 ml boiling concentrated nitric acid until almost dry, then 45 ml of 0.1 N nitric acid was added and heated until the volume was less than 10 ml. This was then diluted to 10 ml with 0.1 N nitric acid and then filtered through a 0.45 µm filter. To find the weight of the extract ($M_{extract}$), the empty centrifuge tubes were weighed and recorded before and after adding the extract to them.

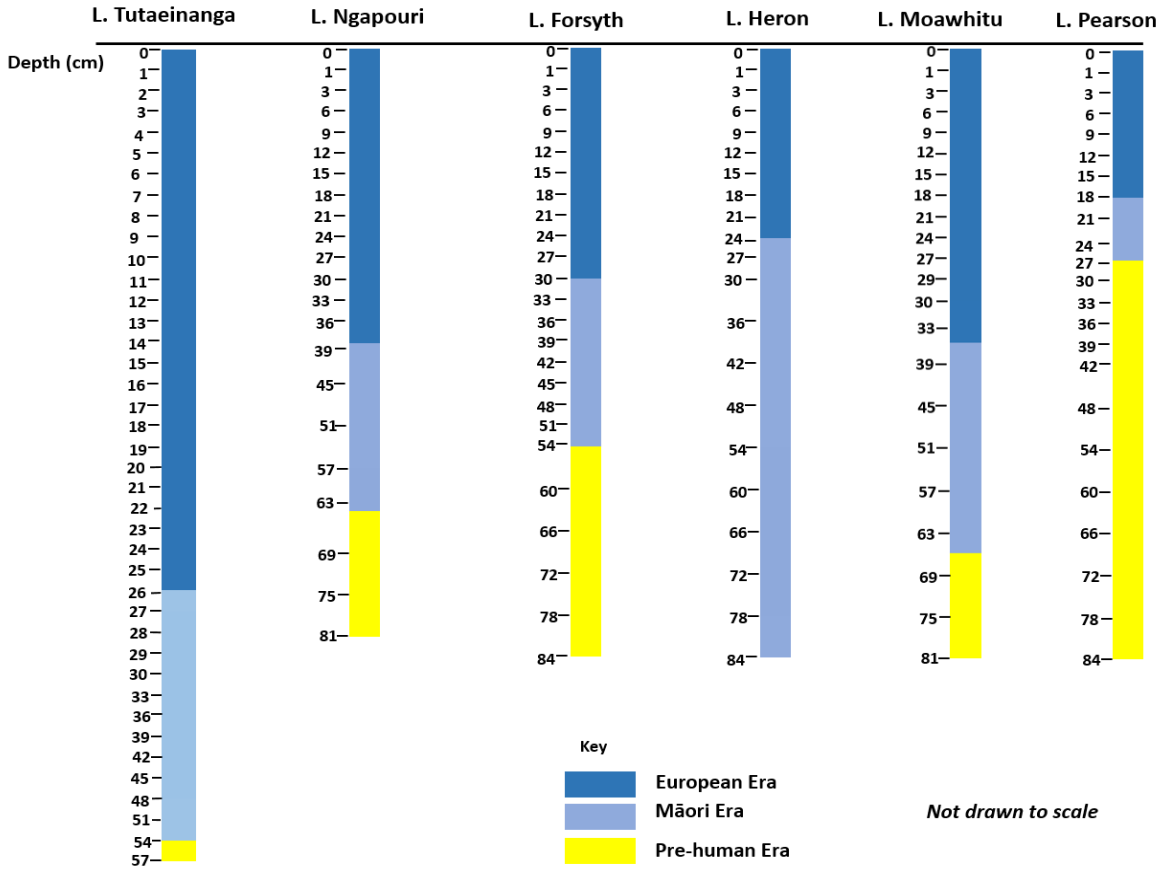

Figure 3-8 Intervals of depth (in centimetres) at which subsamples were taken from the core for geochemical analysis for each lake. Also showing approximate depths for Maori, European and Prehuman perods.

Calculating the dilution factor

Dilution factors are required to convert concentration in the digests back into concentration in the sediment. The dilution factor was calculated by dividing the final weight of the extract by the weight of the sediment used.

$$Dilution\ factor = \frac{M_{extract}}{M_{sediment}}$$ **Equation 1**

where

$M_{sediment}$ = the weight of dry sediment digested for each sample (about 100 mg)

$M_{extract}$ = the final weight of the extract.

3.3.2 Sediment analysis

The digestions were analysed by ICP-OES analysis at the Lincoln University Trace Elements Laboratory to find the concentration of trace elements in the extract ($C_{extract}$). ICP-OES is a technique that is used to detect chemical elements in solutions. The technique uses inductively coupled plasma to produce excited ions or atoms that emit unique spectra (i. e. graph of light intensity as a function of wavelength) based on the characteristics of a certain element. The determination of the type of element is based on the position of the spectral lines and the concentration of the element is directly proportional to the intensity of the line.

The ICP-OES technique has different detection limits for various elements. Detection limits are the lowest concentrations of an element in a sample that can be distinguished from the absence of that element. Lincoln University Trace Elements Laboratory uses an Agilent 5110 SVDS ICP-OES instrument that has detection limits shown in Table 3-4.

Table 3-4 ICP-OES detection limits in the digestion as described by Lincoln University Trace Elements Laboratory, and in the core sediment as calculated from the digestion. (*Detection Limit is quoted for a simple aqueous matrix only – other matrices may not achieve these limits).

ELEMENT	ICP-OES DETECTION LIMIT IN LIQUID ($\mu g/L$)	ICP-OES DETECTION LIMIT IN LIQUID (ppm or mg/L)	DETECTION LIMITS IN DRY SEDIMENTS (mg/kg)
Al	1.0	0.001	0.1
As	5.0	0.005	0.5
Cd	0.3	0.0003	0.03
Cu	0.6	0.0006	0.06
Fe	0.4	0.0004	0.04
Mn	0.05	0.00005	0.005
Pb	3.0	0.003	0.3
Zn	0.3	0.0003	0.03
P	7	0.007	0.7
Cr	7	0.007	0.7
Ni	1.3	0.0013	0.13
V	0.3	0.0003	0.03

Converting extract concentration to sediment concentration

To finally arrive at the concentration of an element in the dry sediment, the concentrations of extract from the ICP-OES analysis were multiplied by the dilution factor, as shown in Equation 1 above.

$$C_{sediment} = C_{extract} \times dilution\ factor$$ **Equation 2**

Where, $C_{sediment}$ is the concentration of an element in the dry sediment and $C_{extract}$ is the concentration of extract from ICP-OES analysis.

3.3.3 Quality control

To ensure quality, standard reference material and blank samples were run in the same way as samples in every digestion batch. Standard reference material (SRM) was used to ensure the validation of data and the accuracy and precision of digestion and analytical methods. The SRM (WEPAL 981) was analysed as part of quality control, and the results indicated that the analytical methods were able to identify and quantify trace element concentrations at appropriate levels. Some samples were replicated (or repeated) to ensure the validity of the first results. The relative error for digestion analysis and ICP-OES analysis were determined to be less than 10%.

Table 3.5 shows results of all blanks. Some elements such as Zn showed some minor level of contamination in the blanks that could be associated with the complex aqueous matrix or the type of water used. The minor contamination, however, was within the relative error. To minimise contamination high purity (deionised) water was used and the equipment was pre-washed in acid, and rinsed well, before and after the experiment.

3.3.4 Determining concentrations of trace elements in other cores of Lake Forsyth/Wairewa

This research also determined concentrations of trace elements of cores that were collected from Lake Wairewa by a PhD student in 2013. These cores were collected from different sampling points to the main core described in section 3.3.2 and Figure 3.4. This was to check if different sampling points within the same lake will yield similar concentrations along the cores. The main core used for this study was taken from the middle of the lake at around F4 while for the other two, one was taken from one end of the lake close to the input rivers at sampling point F11 and the other was taken from the other end of the lake close to the output at sampling point F10 (see Figure 3.5).

The 25 cm sediment cores were collected in March 2013 from Lake Forsyth using a Uwitec 90 mm × 60 cm sediment corer. Sediments from these cores were subsampled at the following intervals (1–5 = 1cm intervals, 5–15 = 2cm intervals and from 15–25 at 5 cm intervals. The cores were then frozen and stored at Lincoln University Waterways Water Quality Laboratory. The digestion and analysis of these sediment were similar to those described in sections 3.3.3 to 3.3.5.

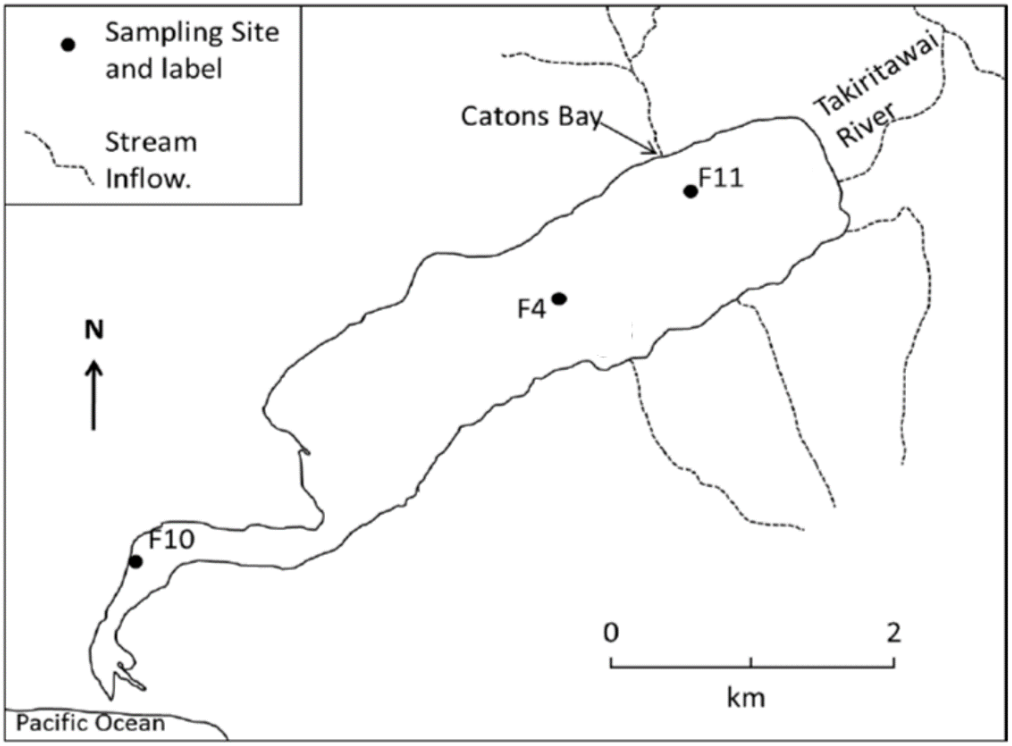

Figure 3-9 showing sediment sampling sites. Cores were taken from analysed cores from F11, F4 and F10. (A. S. Waters, 2016)

Table 3-5 Results of blanks used in the analytical methods (DL = below detectable limit)

	Al (ppm)	As (ppm)	Cd (ppm)	Co (ppm)	Cr (ppm)	Cu (ppm)	Fe (ppm)	Mn (ppm)	Ni (ppm)	P (ppm)	Pb (ppm)	V (ppm)	Zn (ppm)
Lake Tutaeinanga blanks													
BLK1	0.184	DL	0.0004	DL	0.001	0.0038	0.0792	0.0016	DL	0.04	DL	DL	0.1015
BLK1	0.064	DL	DL	DL	DL	0.0029	0.0412	0.0012	DL	0.02	DL	DL	0.0807
Lake Ngapouri blanks													
BLK1	0.141	DL	DL	DL	DL	DL	0.8291	0.0043	DL	0.09	DL	DL	0.2295
BLK2	0.074	DL	DL	DL	0.0033	DL	0.2974	0.0019	DL	0.05	DL	DL	0.085
Lake Forsyth blanks													
BLK1	0.486	DL	DL	0.0011	0.002	DL	0.5837	0.0083	DL	0.03	DL	DL	0.1188
BLK2	0.085	DL	DL	DL	0.0018	DL	DL	DL	DL	DL	DL	DL	0.0141
BLK1	0.053	DL	DL	DL	0.0017	DL	DL	DL	DL	DL	DL	DL	0.022
Lake Pearson blanks													
BLK1	DL	0.0355	DL	DL	DL	DL	0.3972	0.005	0.0052	0.03	DL	0	0.1149
Lake Heron Blanks													
BLK1	0.923	DL	DL	DL	0.0013	DL	0.5797	0.0076	DL	0.03	DL	DL	0.0931
Lake Moawhitu blanks													
BLK1	0.369	DL	DL	DL	DL	0.002	0.7566	0.0063	DL	0.03	DL	0	0.0907
BLK2	0.551	DL	0.0013	0.0011	DL	DL	0.0452	0.0026	DL	0.02	DL	DL	0.0363

3.4 Enrichment factor (EF) and modified pollution index (MPI)

There are several techniques used to estimate the magnitude of trace elements accumulation in sediments(Brady et al., 2015). Calculating an enrichment factor (EF) is the most common technique and is applied to differentiate the trace elements originating from anthropogenic activities and those from natural environmental processes (Selvaraj et al., 2004). The expression of the EF used in this study involves normalising the concentration of trace elements in the sediments, with reference to an element that has zero anthropogenic influence, or has such a high natural concentration that anthropogenic sources have little effect on its concentration (Brady et al., 2015). This makes the EF more specific to anthropogenic contamination, and as a general rule any EF greater than 1 indicates an anthropogenic source of the element. Table 3-3 shows the classes that are used to interpret the values of EFs.

The reference elements that are used to normalise EFs include Al and Fe (Acevedo-Figueroa et al., 2006; Amin et al., 2009; Huang & Lin, 2003; Karbassi et al., 2008; Lin et al., 2008), Mn, Ti, and Sc (Salati & Moore, 2010; Zahra et al., 2014) and Li and Cs (Pereira et al., 2007). Al was used as a reference for this study because it showed relatively stable concentration values along the sediment cores compared to Fe and Mn.

3.5 Calculation of EF

EF was determined as a ratio of concentration of trace elements in sediments to the corresponding concentrations in the background conditions. There are several ways of establishing pristine/background conditions, but the most common is by determining the concentrations of an element in sediments that are found at depths beyond the effects of human activity (Abrahim & Parker, 2002; Forstner & Wittmann, 1979; P. A. Tanner et al., 2000).

For this study, background concentrations (for all lakes except Lake Heron) were calculated by determining the average concentration of trace elements in the prehuman era (as identified by pollen analysis results, Section 3.3.1). The background concentration for Lake Heron was established by determining the average concentrations in the bottom 10 cm of the sediment core (Ma et al., 2016), because the core for Lake Heron was not deep enough to include the prehuman era. This can be justified because the geochemistry of the early settlement of Māori can mostly be equated to prehuman conditions (Stoffers et al., 1983; Wilmshurst et al., 2004).

The following equation was used to calculate the EF.

$$\boldsymbol{EF} = \frac{\left(\frac{C_x}{C_{Al}}\right)_{\boldsymbol{Sample}}}{\left(\frac{C_x}{\mathrm{Al}}\right)_{\boldsymbol{Background}}} \qquad \textbf{Equation 3}$$

where $\left(\frac{C_x}{C_{Al}}\right)_{Sample}$ was the ratio of trace elements concentrations to that of Fe in the sediment after human activities, and $\left(\frac{C_x}{C_{Fe}}\right)_{Background}$ was the corresponding average ratio in sediments deposited before anthropogenic activities commenced.

Average EF

To put into context the Māori, European and very recent enrichment of the trace elements, average values of EF were established. Three types of average EF values were established: the average EF values in the Māori era to establish the enrichment by the Māori settlement, the average EF values in the European era establish the enrichment by the European settlement, and finally the average EF values in the top 3 cm of the sediment core to establish recent enrichments in the intensive farming period.

3.5.2 Calculation of MPI

This study also used a modified pollution index, as described by Brady et al. (2015), which can be used in environments where multiple contaminants are present together. EFs are used to calculate MPI and in this study, EFs of the four elements (Cd, Cu, Zn and As) that are commonly present or used in New Zealand agricultural land use activities, were used to calculate the MPI.

$$MPI = \sqrt{\frac{(\overline{EF})^2 + (EF_{Max})^2}{2}} \qquad \textbf{Equation 4}$$

where $\overline{EF}$ is the average EF of the four elements (Cd, Cu, Zn and As) and EF_{Max} is the maximum EF of the four elements.

Table 3-6 The classes used to interpret the values of EFs and MPI (Brady et al., 2015; Zahra et al., 2014)

CLASS	QUALIFICATION OF SEDIMENTS	EF VALUE (Eqn 3&4)	QUALIFICATION OF SEDIMENTS	MPI VALUE (Eqn4)
0	Unpolluted/enriched	EF <1	Unpolluted/enriched	MPI < 1
1	Slightly polluted/enriched	1 < EF < 3	Slightly polluted/enriched	1 < MPI < 2
2	Moderately polluted/enriched	3 < EF < 5	Moderately polluted/ enriched	2 < MPI < 3
3	From moderately polluted to strongly polluted/enriched	5 < EF < 10	Moderately-heavily polluted/enriched	3 < MPI < 5
4	Strongly polluted/enriched	10 < EF < 25	Heavily polluted/enriched	5 < MPI < 10
5	From strongly polluted to extremely polluted/enriched	25 < EF < 50	Severely polluted/enriched	10 < MPI
6	Extremely polluted/enriched	EF > 50	-	-

3.6 Determining molar ratios of Mn/Fe, Cu/Pb, Zn/Pb and molar relationship of Cd and P.

The molar ratios of Mn/Fe, Cu/Pb and Zn/Pb were determined to help in interpreting the results of the concentrations of the trace elements along the cores.

Fe is scavenged by sulphide ions to form Fe sulphide under anoxic conditions while Mn remains mobile (Salomons et al., 1987). Other elements such as Cd also form sulphides under anoxic conditions (Salomons et al., 1987). This understanding can help to interpret the trends of trace elements when Mn/Fe ratio are plotted. Also literature shows that Mn has an inverse relationship to Cd in sediment cores (Nolting et al., 1999); when Mn shows an

increase in the upper part of the core due to redox cycling, Cd show a decrease (Chaillou et al., 2002; Duinker et al., 1982; Gendron et al., 1986; Gobeil et al., 1987). Therefore when Mn is normalised to Fe, it can help to interpret the behaviour of Cd in the sediment cores.

Cu/Pb and Zn/Pb were important in differentiating the source of Cu and Zn as being either from urban or rural land use. Cu, Zn and Pb have constant ratios in undisturbed environments (Weng et al., 2003). Since the main anthropogenic sources of Pb are from urban environments only, Cu and Zn are expected to increase while Pb remains constant, unless there is an influence from an urban area, road runoff or all of them are undisturbed.

The molar relationship of Cd and P was also determined to understand the relationship of Cd and P in freshwater sediment cores. Literature shows that Cd is closely related to the biogenic cycle just like P (Boyle et al., 1976; Bruland et al., 1978; de Baar et al., 1994; Pace et al., 1987); and their relationship is important in biogeochemistry of Cd in the sediment cores. The relationship of Cd to P would also help to establish if the concentrations of P in the sediments are coming from agriculture inputs or from natural cause. Natural sources of P have low concentrations of Cd compared to fertiliser inputs (McLaughlin & Singh, 1999).

The following equation was used to convert the concentration of trace elements in the sediment cores determined in section 3.3 to number of moles.

$$\boldsymbol{Moles\ of\ X\ (moles/kg)} = \frac{\boldsymbol{Weight\ of\ X\ (g/kg)}}{\boldsymbol{atomic\ weight\ of\ X}} \qquad \textbf{Equation 5}$$

where X is the trace element of interest, weight of X is the concentration of the trace element in the sediment cores at a particular depth and atomic weight of X is the mass of an atom of the studied trace element.

After finding the number of moles of the Fe, Mn Cu, Zn and Cd and P in the sediment cores, ratios of Mn/Fe, Cu/Pb and Zn/Pb and relationship of Cd and P were plotted in graphs and have been presented Chapter 4.

Chapter 4

Results

4.1 Description of lake sediment cores

4.1.1 Lake Tutaeinanga core

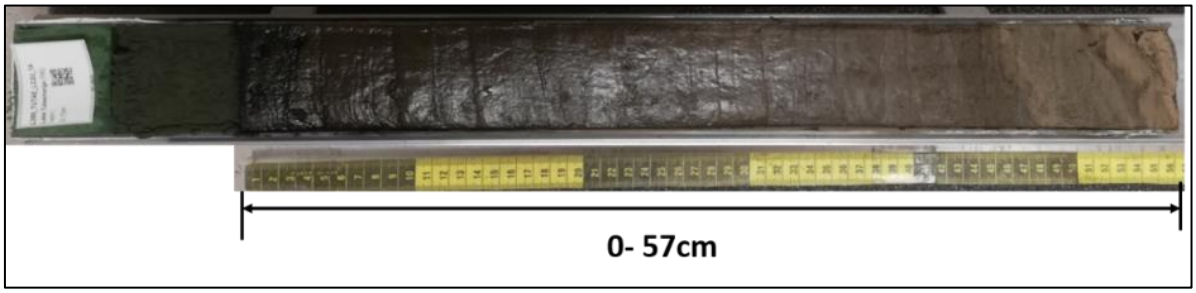

Figure 4-1 Lake Tutaeinanga sediment core (57 cm long) showing black mad in the top part of the core, brown coloured core in the middle and light brown/sandy coloured at the bottom. The foam at the top was used to hold and protect the core from mixing with contaminants.

A 57-cm-long core was collected at Lake Tutaeinanga and the coring could not continue beyond this depth because of the dense thick volcanic ash, which may be associated with the Kaharoa volcanic eruption that occurred around AD 1314 at Mount Tarawera (Hogg et al., 2012). Table 4.1 shows the description of the sediment core as it was observed by the Lakes380 project team on the day of splitting the core.

Table 4-1 Description of Lake Tutaeinanga sediment core

DEPTH (cm)	DESCRIPTION OF LAKE TUTAEINANGA CORE
0–4	Black mud with brown mud bands (about 1 mm thick)
4–13.5	Brown mud with black/smears.
13.5–19.5	Dark brown mud
19.5–43	Light brown mud with faint smears of brown mud (light mud at 22.5 cm and a dark patch at 40.5 cm)
43–45.5	Brown with dark brown bands
45.5–47	Light brown with a sandy light brown band at 47 cm
47–53.5	Mud brown with black specks of mud and light brown bands
53.5–54.5	Dark brown band
54.5– 56.6	Light brown with dark brown bands
56.5–57	Very light brown/sandy coloured

4.1.2 Lake Ngāpouri core

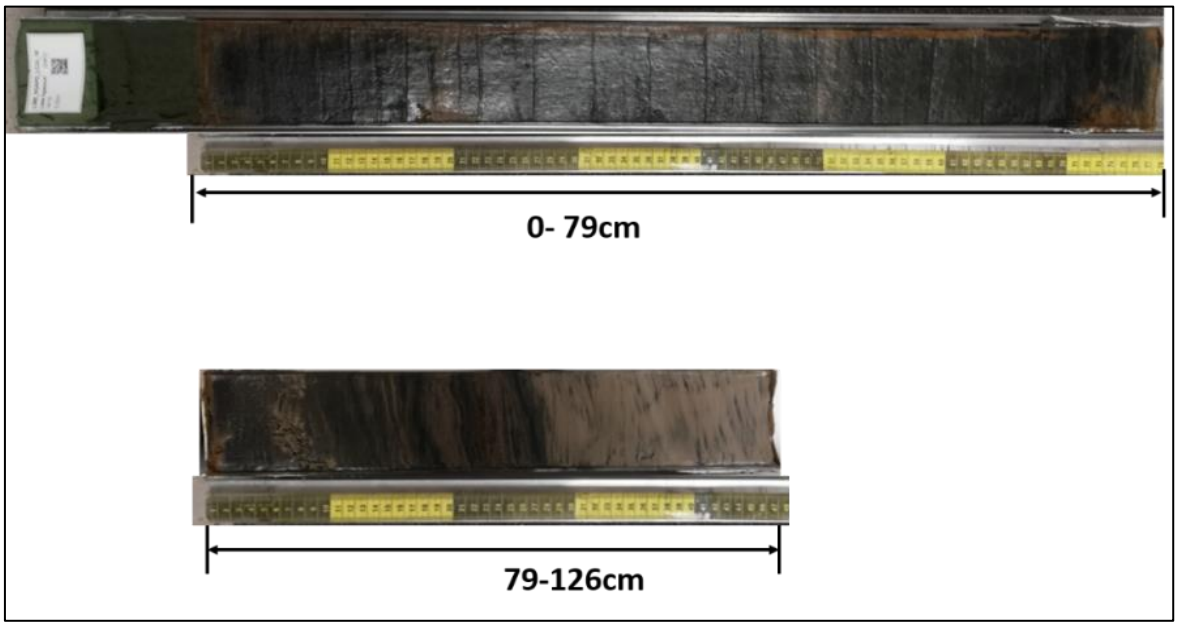

Figure 4-2 Lake Ngāpouri core (126 cm long) showing a general colour of dark black with smears of light brown mud and and one side of orange-brown colour (showing signs of oxidation). The foam at the top was used to hold and protect the core from mixing with contaminants.

A 126-cm-long core was collected from Lake Ngāpouri and the core was generally dark black with smears of light brown mud throughout. One side of the core had an orange brown colour (sign of oxidation) up to the depth of 73.5 cm (the distribution of this brown colour indicates that oxidation may have happened after coring). This could not influence the results of the sediments as the subsamples were taken from the middle of the core. More details of this core are in Table 4-2.

4.1.1 Lake Forsyth (Te Roto o Wairewa) core

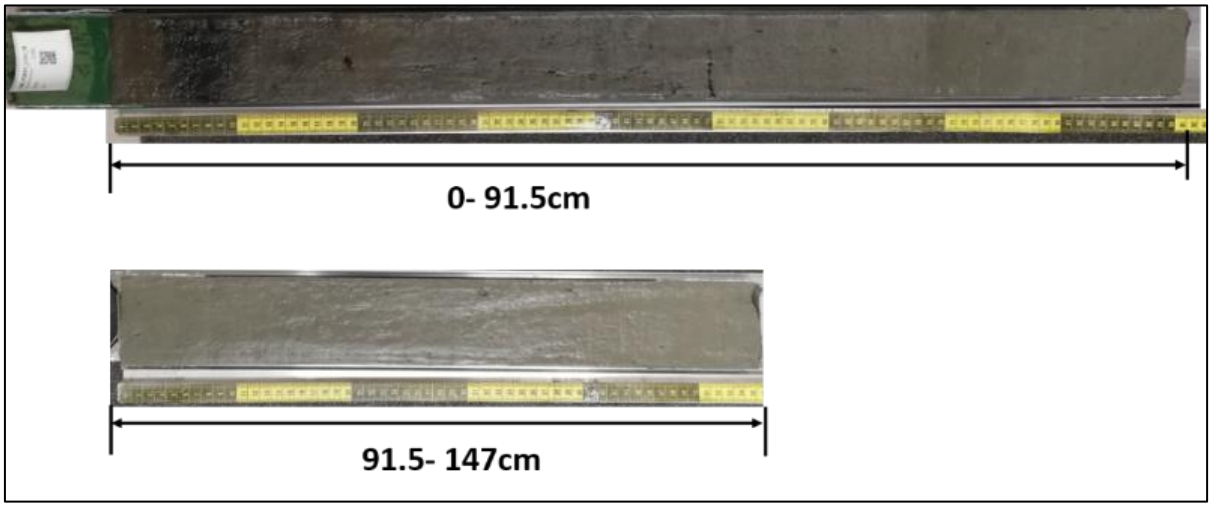

Figure 4-3 Sediment core for Lake Forsyth (147 cm long) showing general colours of brown greyish mud or greyish brown mud with smears of black colour throughout. The foam at the top was used to hold and protect the core from mixing with contaminants.

Table 4-2 Description of Lake Ngāpouri sediment core

DEPTH (cm)	DESCRIPTION OF LAKE NGĀPOURI CORE
0-0.5	Orange brown band of mud (oxidation)
0.5-73.5	Orange brown mud on one side of the core (sign of oxidation that might have happened after coring)
0.5–19.5	Very dark black mud with smears of light brown mud throughout
19.5–20.5	Band of light brown mud with blotches of black mud
20.5–27	Black mud with smears of light brown mud throughout
27–40	Dark grey/charcoal coloured mud with smears of greyish brown mud throughthout
40–51	Black mud with smears of dark grey mud throughout
51–52	Band of light brown mud
52–65	Smears of dark grey and black mud
65–71	Black mud, smears of dark grey mud
71–78.5	Bands of black and dark grey mud
78.5–79	Orange mud band (oxidation)
79–80	Thin brown/orange band of mud (could be oxidation that might have happened after coring the core)
80–85.5	Black mud with faint dark grey bands
85.5–90	Rocks, gravelly texture, grey/black mud
90–93	Grey/ black band starting to alternate with light brown/grey mud
93–96	Banding of grey black with grey/brown more distinct
96–104	Alternate banding continuing but with rough texture (gravelly sandy)
104–106	Alternate banding is smooth, more grey/black banding than brown/grey
106–126	Smooth, mainly grey/brown all the way with a few patches of grey dark bands

The core from Lake Forsyth that was used for this study was 147 cm long and had general colours of brown greyish mud or greyish brown mud with smears of black colour throughout. At the depth of 5 to 10.5cm the core was dark grey (charcoal black) mud with smears of brown colour. More details are shown in Table 4-3.

Table 4-3 Description of Lake Forsyth (Te Roto o Wairewa) core

DEPTH (cm)	DESCRIPTION OF LAKE FORSYTH CORE
0–5	Brown greyish mud
5–10.5	Dark grey /charcoal black mud with smears of brown mud
10.5–91.5	Brown greyish mud with smears of black throughout Lots of black smears at 39.5 cm and 45.5 cm Little organic looking patch at 19.5 cm and at 50 cm
91.5–147	Greyish brown mud with black smears of mud throughout Gradual fade from greyish brown to slightly browner mud Significant patches of black mud at 99.5 cm , 105.5 cm and 107.5 cm, 128.1 cm and 143.5 cm Speck of organic matter at 135.5 cm

4.1.2 Lake Pearson core

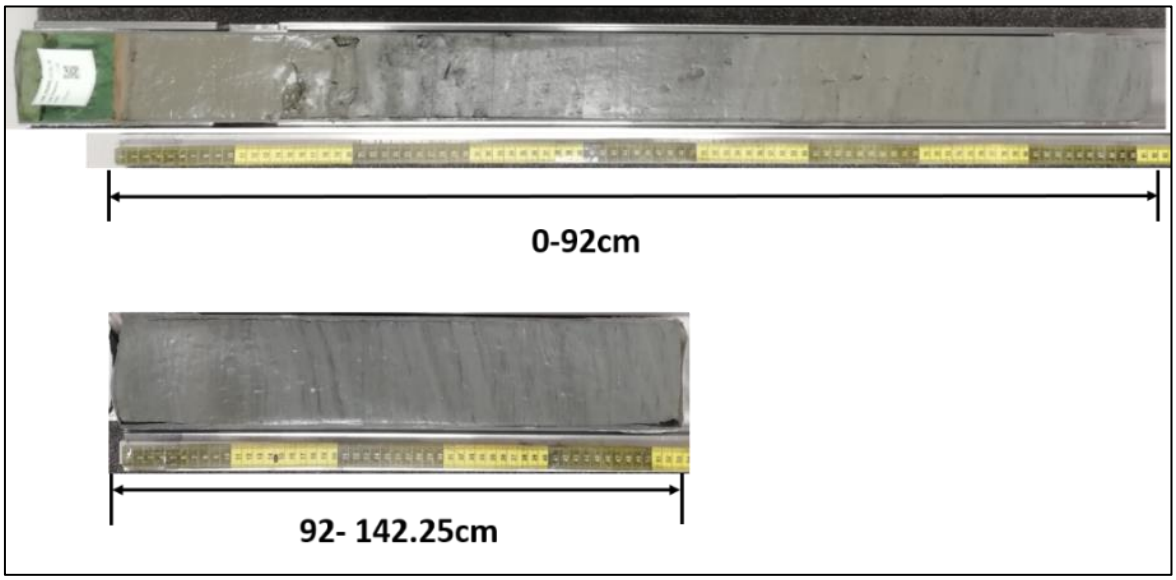

Figure 4-4 Lake Pearson sediment core (142.25 cm core) showing a general colour of grey mud. The foam at the top was used to hold and protect the core from mixing with contaminants.

A 142.25-cm-long core was collected from Lake Pearson. The core had a general colour of grey with faint specks of black mud and light grey mud. An oxidation layer was seen in the first (top) 0.5 cm. More details in table 4-4.

Table 4-4 Description of Lake Pearson core

DEPTH (cm)	DESCRIPTION OF LAKE PEARSON CORE
0–0.5	Oxidation layer (orange brown mud)
0.5–14	Greyish brown mud with one band of black/charcoal grey mud at 1 cm
14–34	This section looks like it has a lot of radiocarbon (wooden materials) 14–21.5 cm had greyish brown mud 21.5–29 cm grey mud with faint 1-cm-thick bands of slightly lighter grey mud 29–33 gradient from dark grey to lighter grey.
33–92	Alternating bands of grey and greyish brown mud Bands on diagonal angle (higher on left side of core, lower on right side of core) Black specks of mud throughout
92–97	Grey mud, faint specks of dark mud throughout
97–100.5	Gradient from grey to brownish grey mud
100.5 –105	Grey mud with faint smears of light grey mud and black specks of mud
105–127.5	Diagonal (higher on right hand side, lower on left hand side) bands of brown mud at 109 cm, 110.5 cm, 112.5 cm, 122.5 cm and 127.5 cm (measured from left side) Grey and light grey mud with black lines/specks of mud throughout
127.5–144.5	Grey mud with black specks of mud throughout, faint diagonal bands of grey mud

4.1.3 Lake Heron core

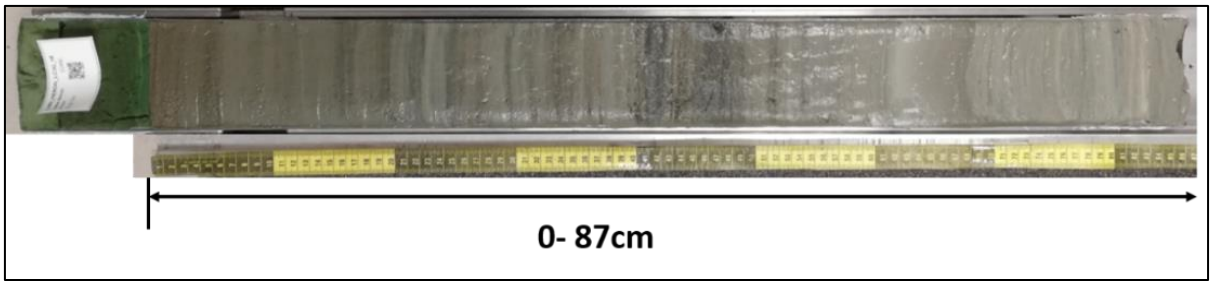

Figure 4-5 Lake Heron sediment core (0–87cm long) showing alternating bands of light grey or dark grey and black or brown mud. The foam at the top was used to hold the core during coring and to protect the core from mixing with contaminants.

An 87-cm-long core was taken from Lake Heron and the core had a general colour of alternating bands of light grey/dark grey and black or brown mud. The oxidation layer was in the top 0.5cm and the core had a band of organic matter at a depth of 40 to 40.5 cm. More details are shown in Table 4-5.

Table 4-5 Description of Lake Heron sediment core

DEPTH (cm)	DESCRIPTION OF LAKE HERON CORE
0–20	Alternating bands of brownish grey mud and faint black mud One orangey brown band (sign of oxidation) in the top 0.5 cm
20–40	Alternating bands of light grey, black and brown mud. Very brown band at 37 cm, black bands at 22 cm, 24.5 cm, 33.5 cm and faint black bands at 25.5 cm, 27cm,29.5 cm and 36.2 cm
40–40.5	Organic matter band
40.5–49.5	Black /charcoal coloured mud with brown band and at 42.5– 44.5 cm organic matter throughout
49.5–61	Alternating bands of light grey and dark grey bands. Black band at 51.5 cm
61–68	Smooth mud, fades from very light grey to brownish grey
68–87	Alternating bands of light grey and brownish grey, black bands at 77.5 cm and 80.5 cm

4.1.4 Lake Moawhitu core

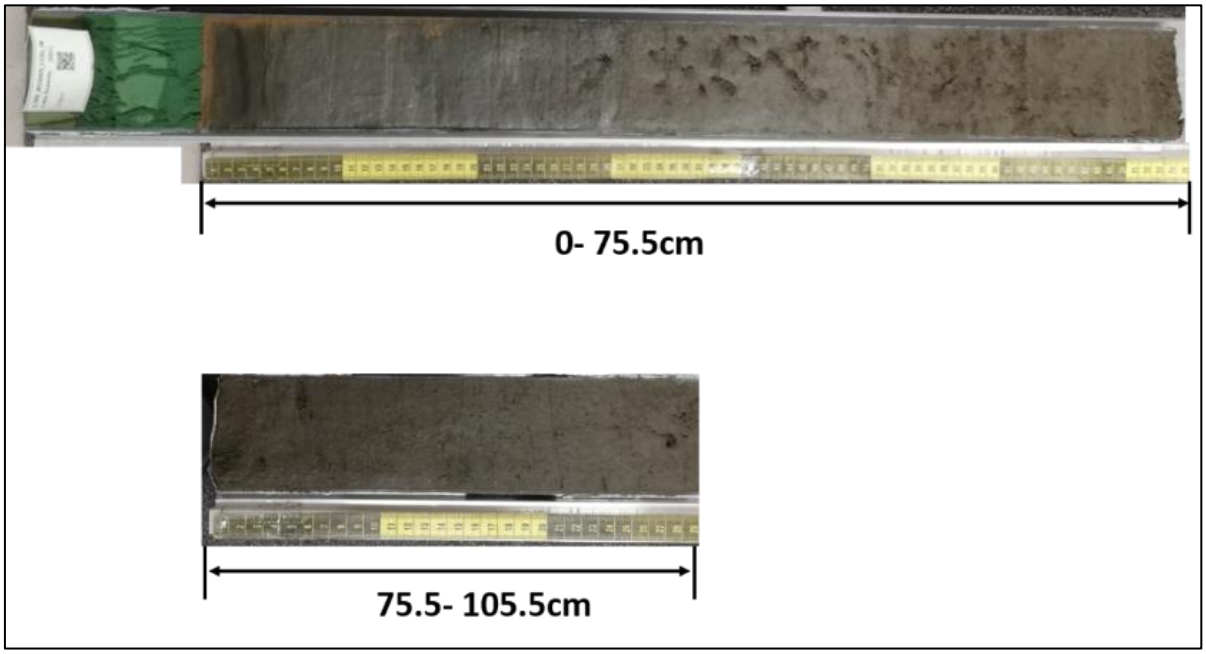

Figure 4-6 Lake Moawhitu sediment core (105.5 cm long) showing dark brown and greyish brown mud with smears of black mud. The foam at the top was used to hold the core during coring and to protect the core from mixing with contaminants.

This core was 105.5 cm long and had general colours of dark brown and greyish brown with smears of black mud. Oxidation layer was in the top 0.5 cm and there was oxidised mud on the right side of the core up to the depth of 17 cm. More details are shown in Table 4-6.

Table 4-6 Description of Lake Moawhitu sediment core

DEPTH (cm)	DESCRIPTION OF LAKE MOAWHITU CORE
0–0.5	Orange brown band of mud (oxidation)
0–21.5	Oxidation layer on the left side of the core
0–5.5	Dark greyish brown mud with bands of black mud
5.5–14.5	Greyish brown mud with faint smears of black mud and oxidised mud up to 17 cm on the right side
14.5–22	Dark brown mud with very faint streaks of grey mud and oxidised mud
22–25.5	Faint gradient to a dark brown mud slightly grey at 22.5 cm and 30.5cm
25.5–75.5	Dark brown mud throughout
75.5–105.5	Dark brown mud throughout, slightly sandy texture at 78 cm and at 99 cm, organic specks throughout

4.2 Concentration of trace elements in lake sediment cores

This section presents results of methods described in section 3.3 of Chapter 3. The distribution of trace elements for each lake is described in section 4.2.1 to 4.2.6, and shown in Figures 4.7 and 4.8. Raw data for all trace elements analysed is given in Appendix A. For each lake the trace elements have been considered in two groupings: those that are known to be derived from common agriculture land use activities (Cd, Cu, Zn, As and P), and those which that provide supporting information on trace element source or processes affecting trace element distribution. Those that are common from agriculture land use are presented in Figure 4.7 and those that may provide supporting information are presented in Figure 4.8.

Figures 4.7 and 4.8 also show the approximate depth corresponding to the arrival of Māori and of Europeans, based on pollen and charcoal analysis (refer to Methods in section 3.3.1 for details on this dating method).

4.2.1 Concentration of trace elements in Lake Tutaeinanga

All the agriculturally relevant trace elements in Lake Tutaeinanga (Fig 4.7) show a steady increase in concentration after the estimated date of the arrival of the Europeans (around 1840). In the case of As, Zn and Pb, however, concentrations do not greatly exceed those present in the oldest sediment in the core. Minimum concentrations occur in the mid-core region.

Other elements, Fe, Al, Mn and Cr also show this type of distribution (Fig 4.8) with relatively high concentration in the bottom 7 cm (between 57 cm and 50 cm) and then lower concentrations until the date of the arrival of the Europeans, after which they start to increase again. In the case of Al, Mn and Cr there is less pronounced enrichment, but erratic concentrations in the recent sediments. Ni shows a distribution similar to that of Cu, Cd and P.

Vanadium, on the other hand, does not appear to be elevated in the recent sediments, relative to during Māori land use activities, but is high in sediment deposited close to the time of European arrival.

4.2.2 Concentration of trace elements in Lake Ngāpouri

Copper and zinc show a rise in the concentration after the depth of 38 cm, which is estimated to be around the dates when the Europeans arrived in New Zealand. Phosphorus shows similar trend but with erratic distribution in the Māori and European eras. Cd concentration rises with the deeper depth. There are relatively higher concentrations of Cd in the prehuman and Māori era compared to European era.

Arsenic (As) shows an erratic trend, with deeper concentrations (in prehuman and Māori era) being relatively higher than those in the top of the core (in the European era). Another notable observation for both Lake Ngāpouri and Lake Tutaeinanga is that they have relatively higher natural concentrations of As and Zn compared with other lakes.

Iron shows similar distribution to Cd. There are also very low concentrations of Fe and Mn in the top 1 cm of the core. Other elements; Al, Cr, V and Pb have similar distributions in the European era; they all have constant concentrations (little variation) in the upper layers. Ni on the other hand, shows a similar trend to Cu and P.

4.2.3 Concentration of trace elements in Lake Forsyth (Te Roto Te Wairewa)

Cadmium in Lake Forsyth starts at the bottom with higher concentration that started to decrease in the Māori era to reach its minimum concentration (0.9262 mg/kg ± 5%) at the depth of 54 cm, which is estimated to be where the evidence of Māori settlement started to be seen. Then, Cd increased up to the concentration of 2.2526 mg/kg (± 5%) at the depth of 42 cm where it started to decrease gradually with erratic distribution in the upper layer.

Copper, zinc, and lead started with high concentrations at the bottom and then decreased gradually through the Māori era and European era until around the depths between 25 cm and 15 cm, from which they started increasing up to the top surface. On the other hand, P has uniform concentration in the bottom sediment until the depth of 25 cm, after which the concentration start to rise steeply.

Arsenic shows relatively uniform concentration in the prehuman and Māori era. Then, there is a rise soon after the arrival of Europeans to reach the maximum concentration at a depth of 24 cm and after this the concentrations became constant again. Other elements; Fe, Mn, Cr, Ni and V showed a similar trend where their concentrations in the sediments decrease with the deeper depths.

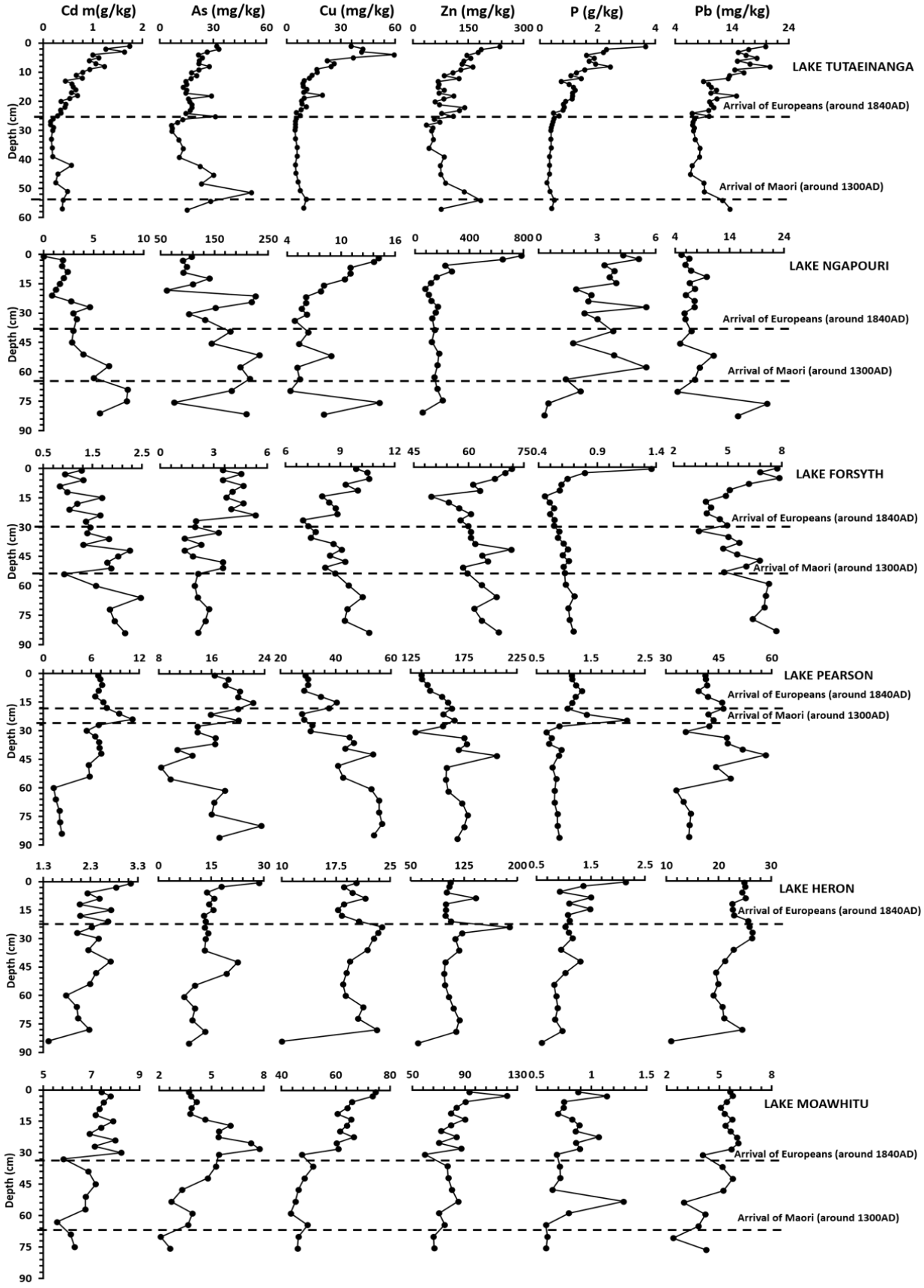

Figure 4-7 Concentration of agriculturally-relevant trace elements; Cd, As, Cu, Zn, P and Pb in sediments (±10), as a function of depth, in six lakes studied. It also shows the approximate depth corresponding to the arrival of Māori and Europeans and prehuman conditions.

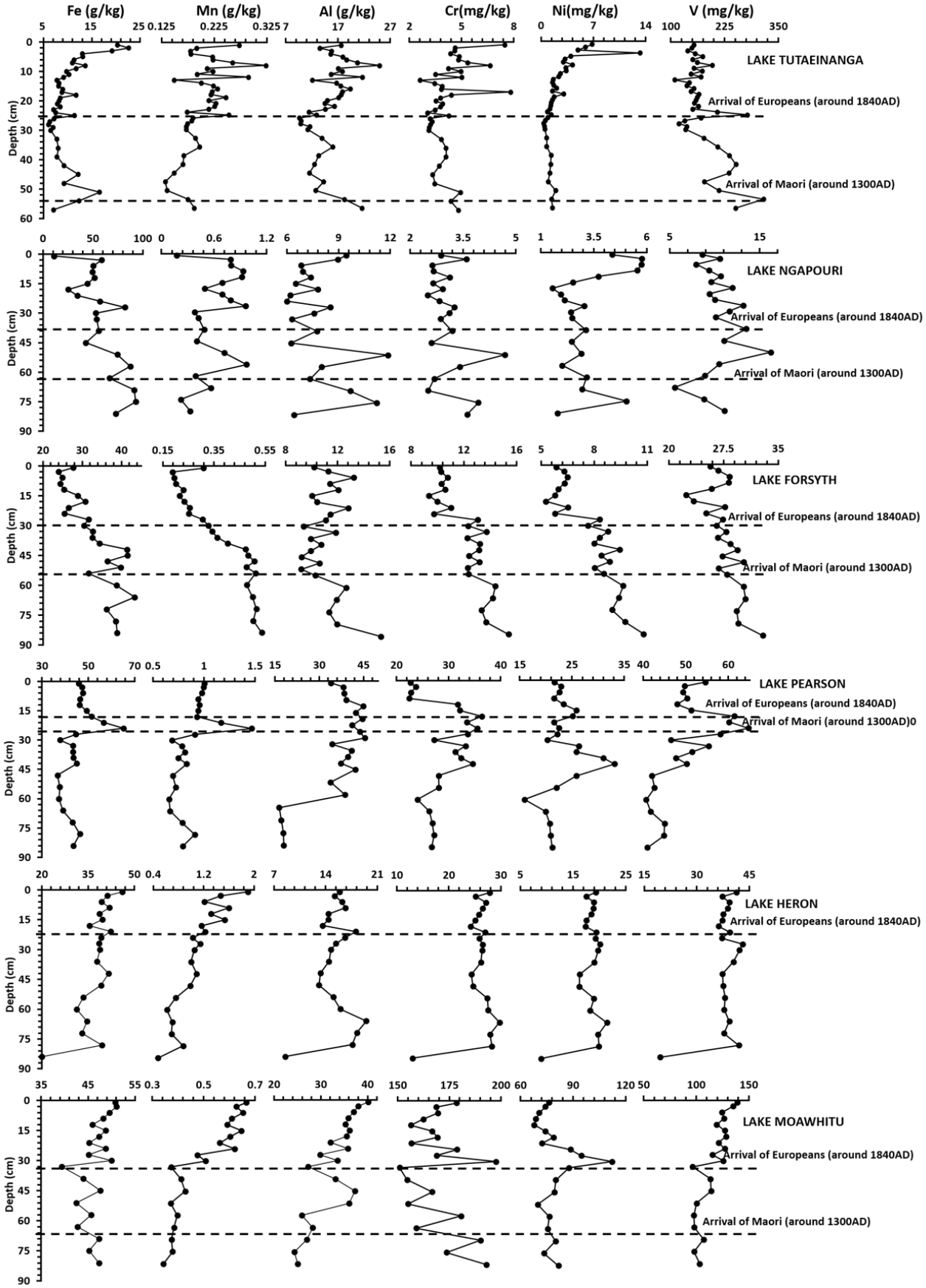

Figure 4-8 The concentration of trace elements that may provide supporting information on trace element source and distribution (Fe, Mn, Al, Cr, Ni and V) in sediments (±10), , as a function of depth, in the six lakes studied. It also shows the approximate depth corresponding to the arrival of Māori and Europeans and prehuman conditions.

4.2.4 Concentration of trace elements in Lake Pearson

In Lake Pearson sediment cores, Cd and P show a similar trend; they have relatively low values in the prehuman era, they rise and decrease within the Māori era and then show constant concentrations in the European era. On the other hand, Cu and Zn concentrations decrease with the depth. Arsenic starts with high concentrations at the bottom, and decreases to reach its minimum concentration at the depth of 48 cm from which it rises up to the depth of 15 cm in the European era. In the European era, As show a minor decrease up to the top of the sediment core.

Iron, manganese and lead show almost similar distributions to Cd and P. Ni concentrations rise and fall within the prehuman era and then show constant concentrations in both the Māori and European era. Aluminium and chromium show similar distribution, they start with low values which increase until the estimated date of the arrival of Europeans, from which they decrease gradually.

4.2.5 Concentration of trace elements in Lake Heron

All the elements in Lake Heron have a significant low value for the last point at the depth of 84 cm which is different to the trends of the concentrations of the entire core. The concentrations of Cd, As, and P in Lake Heron sediment core show minor increases in both Māori and European era and then a sudden rise in the top 10 cm.

Copper and lead concentrations show moderate variations within the Māori era and then show uniform concentrations in the European era. On the other hand, Zn shows similar sediment concentrations along the core in both the European and Māori eras except for the last point at the bottom, which show a lower concentration.

Other elements show similar distributions to the elements described above. Iron and manganese show almost similar distributions to Cd, P and As, while Al shows a similar trend to Cu and Pb, and Cr, Ni, and V show similar distribution to Zn.

4.2.6 Concentration of trace elements in Lake Moawhitu

In Lake Moawhitu, the agriculturally relevant trace elements Cd, Cu and Zn show similar trends, where they gradually rise along the core from prehuman era to European era. Arsenic rises in the Māori era and show a gradual decrease in the European era. P shows an erratic trend in both the Māori and European eras.

For this lake, other elements show similar distributions to the agriculturally relevant trace elements described above. The elements; Fe, Mn, Al and Pb show similar distributions to Cd, Cu and Zn, while Ni shows a similar trend to As. Cr shows an erratic trend.

4.2.7 Results of the concentrations of trace elements in other cores of Lake Forsyth/Wairewa

This section shows the results of the concentrations of trace elements in the other cores of Lake Forsyth/Wairewa described in section 3.6. The results are presented in Figure 4.9. The results show higher concentrations of trace

elements at sampling point F10 than at sampling point F11. The concentration of trace elements in sediment core F10 are also higher than those in the main core presented in Figure 4.7.

The core at sampling point F10 shows that all trace elements had relatively stable concentration throughout the core except in the top 1 to 2 cm where they rose abruptly. The core at F11 had trace elements with different trends of concentrations. Cd was stable throughout the core except in the top 1 cm where it rose abruptly. P rose from 0.3817 g/kg ±10% at the bottom of the core to 0.5323 g/kg ±10% at the top of the core. As, Cu, Zn and Pb show relatively stable concentrations throughout the core with some fluctuations.

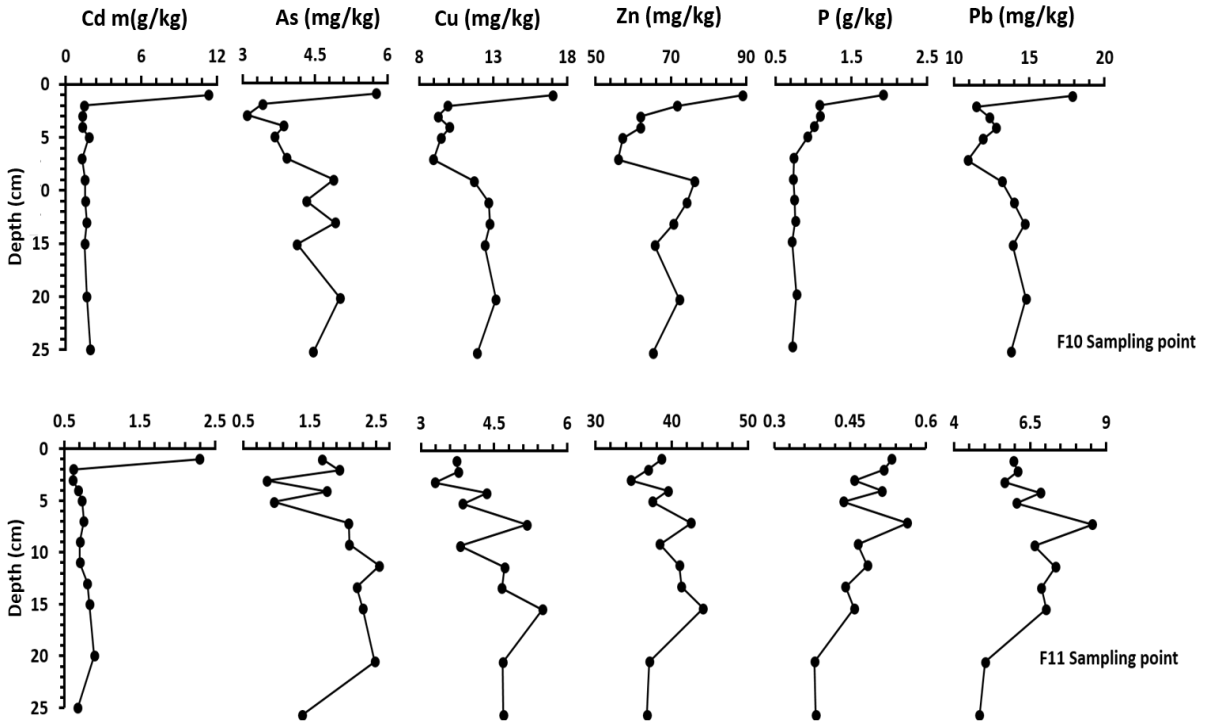

Figure 4-9 Concentrations of trace elements in other cores of Lake Forsyth/Wairewa. Showing results of cores taken at sampling point F10 close to the output and sampling point F11 close to the input.

4.3 Enrichment factors and modified pollution index (MPI) results

This section presents and describes the results for EFs of agriculturally relevant trace elements calculated using Equation 3 in section 3.4. It also presents the average EFs calculated for values in the Māori era, European era and the top 3 cm. The EFs are presented in Figure 4.10 and the average EFs for the Māori era, European era and top 3cm values are presented in Table 4.7. Raw data for all EFs is given in Appendix B. The EF values are described below and are based on Table 3.6, which shows the classes that are used to interpret the EF values.

4.3.1 EF values in Lake Tutaeinanga

All elements are enriched in Lake Tutaeinanga: Cd, P and Cu values show that they were moderately to strongly enriched/polluted in the top 3 cm with average values ranging from 5 to 10, while Zn and Pb have EF values of around 2 in the top 3 cm of the core, which means they are slightly enriched. Arsenic (As) values on the other

hand, show that it is moderately polluted in the top 3 cm but strangely the deepest point at a depth of 51 cm in the Māori era shows the EF value of 6.24±10%, which means it is moderately to strongly polluted/enriched.

4.3.2 EF Values in Lake Ngāpouri

Zinc values show that it is slightly enriched along the core in the Māori and European era, except in the top 3 cm, where it is moderately to strongly enriched/polluted. Phosphorus shows an erratic trend of EF values along the core and all the EF average values for the Māori era, European era and top 3 cm are within the moderately polluted class. Cadmium and lead are not significantly enriched throughout the core, with Cd showing very low values in the top 3 cm. Copper is slightly enriched throughout the Māori and European era while As is slightly enriched in the Māori and European era and it is not enriched in the top 3 cm.

4.3.3 EF Values in Lake Forsyth and Lake Moawhitu (coastal lakes) sediment cores

Almost all the elements in Lake Forsyth and Lake Moawhitu are slightly enriched except Cd and As (Cd in both lakes and As in Lake Moawhitu only) which show very low values that are described as not enriched in the EF class in Table 3.3.

4.3.4 EF values in Lake Pearson and Lake Heron (highland lakes) sediment cores

The agriculturally related elements; Cd, As and P are slightly enriched in both lakes while Cu is not enriched in both lakes. Lead and Zinc are slightly enriched in Lake Heron and not enriched in Lake Pearson.

Table 4-7 shows the average EF for values in the top 3 cm depth, the European era and Māori era relative to prehuman conditions. The table presents average EFs for six trace elements: Cd, As, Cu, Zn, P and Pb calculated using Equation 3.

Element	Era/depth	Tutaeinanga	Ngāpouri	Forsyth	Pearson	Heron	Moawhitu
Cd	**Top 3 cm**	**5.00**	**0.14**	**0.66**	**1.28**	**1.37**	**0.75**
	European era	**2.34**	**0.36**	**0.72**	**1.18**	**1.16**	**0.83**
	Māori era	**1.07**	**0.65**	**1.10**	**1.59**	**1.04**	**0.81**
As	Top 3 cm	3.06	0.63	2.07	1.00	1.77	0.88
	European era	1.96	1.07	1.86	1.00	1.27	1.38
	Māori era	2.15	1.41	1.27	0.87	1.06	1.13
Cu	**Top 3 cm**	**5.09**	**1.54**	**1.23**	**0.54**	**0.97**	**1.02**
	European era	**2.25**	**1.20**	**1.02**	**0.53**	**0.97**	**0.99**
	Māori era	**0.89**	**0.78**	**1.10**	**0.43**	**1.05**	**0.80**
Zn	Top 3 cm	1.95	5.09	1.29	0.69	1.02	1.02
	European era	1.08	2.02	1.06	0.67	1.04	0.89
	Māori era	0.88	1.21	1.23	0.69	1.13	0.91
P	**Top 3 cm**	**7.57**	**4.85**	**1.93**	**1.17**	**1.87**	**1.12**
	European era	**3.62**	**4.49**	**1.07**	**1.09**	**1.44**	**1.07**
	Māori era	**1.42**	**3.72**	**1.17**	**1.54**	**1.09**	**1.18**
Pb	Top 3 cm	1.70	0.43	1.21	0.83	1.19	1.07
	European era	1.21	0.63	0.84	0.77	1.15	1.17
	Māori era	0.98	0.63	0.98	0.73	1.07	1.06

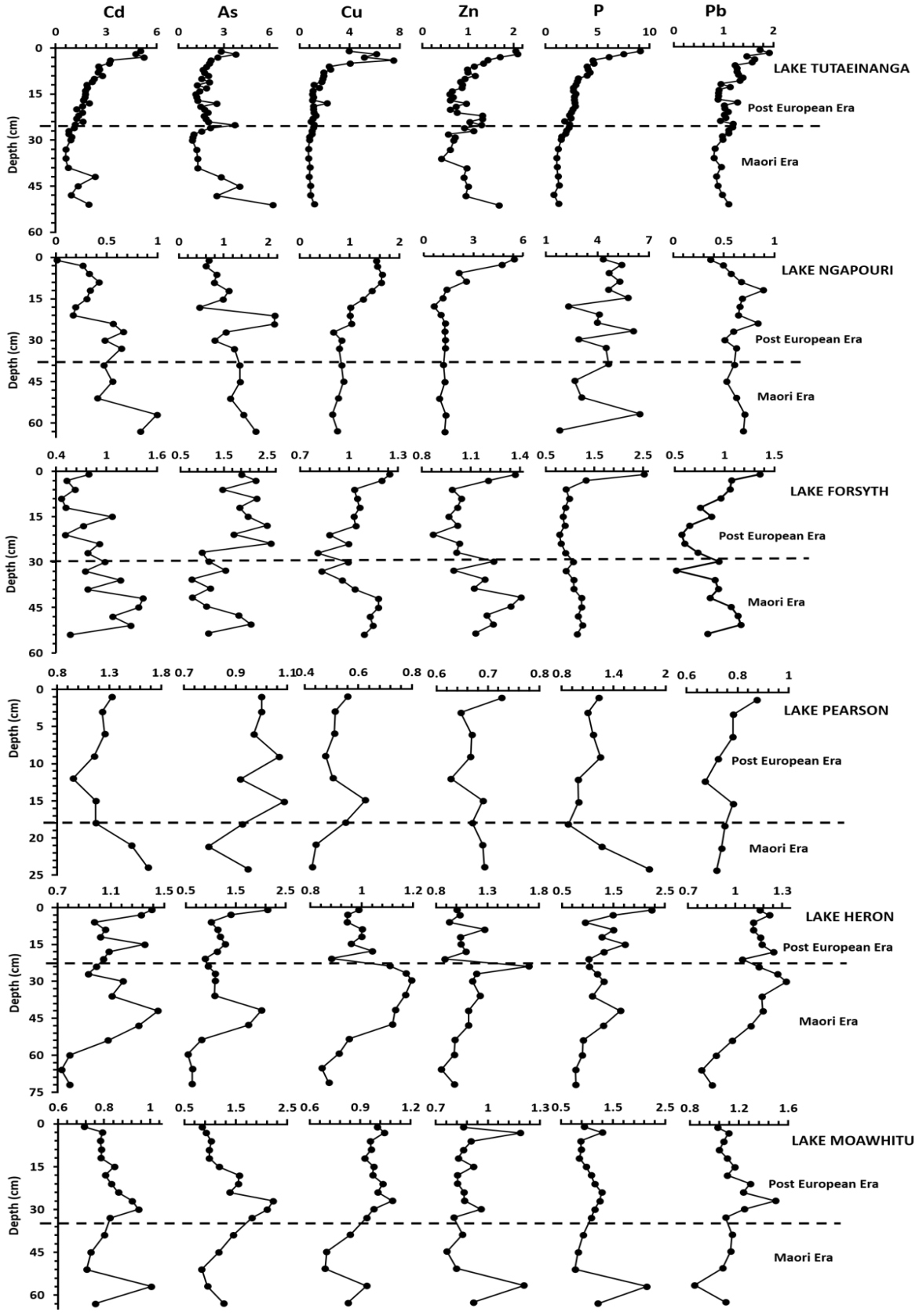

Figure 4-10 EF values of the agriculturally related trace elements (Cd, Cu, As, Zn and P) and Pb in the six lakes studied. It also shows the approximate depth corresponding to the boundary of the Māori era and European era.

4.4 Modified pollution indices (MPI)

This section shows results for MPI in Table 4.8 as calculated using Equation 4, where the EFs of the four elements (Cd, Cu, Zn and As) that are commonly present or used in New Zealand agricultural land use activities were used to calculate the MPI.

By using a modified pollution index to assess multiple-element enrichment in the six selected lakes, it is clear that all lakes are slightly enriched except Lake Ngāpouri and Lake Tutaeinanga (lakes in low-lying areas). Both these lakes show that they are moderately to heavily enriched/polluted in the recent sediments in the top 3 cm of the core.

Table 4-8 MPI values as calculated using Equation 4.

Era/ depth	Tutaeinanga	Ngāpouri	Forsyth	Pearson	Heron	Moawhitu
Top 3 cm	**4.48**	**3.83**	**1.74**	**1.10**	**1.55**	**0.97**
European Era	**1.93**	**1.65**	**1.55**	**1.03**	**1.19**	**1.21**
Māori Era	**1.76**	**1.23**	**1.23**	**1.29**	**1.10**	**1.03**

4.5 Results of molar ratios of Mn/Fe, Cu/Pb, Zn/Pb and molar relationship of Cd and P.

The following section shows results of molar ratios of Mn/Fe, Cu/Pb, Zn/Pb and molar relationship of Cd and P, as described in section 3.5 in Chapter 3. The graphs for these ratios are presented in Figures 4.11 and 4.12, and described in sections 4.4.1 to 4.4.3 below. The calculations results are shown in Appendix C in tables tableC.1 to tableC.6.

4.5.1 Mn/Fe Ratio

There are almost constant ratios of Mn/Fe throughout the cores of Lake Forsyth, Lake Pearson and Lake Moawhitu. In Lake Ngāpouri and Lake Heron, the Mn/Fe ratios rose in the top 30 cm of the cores, while in Lake Tutaeinanga, the ratios decreased in the top 10 cm. The ratios in Lake Tutaeinanga decreased at the bottom of the core and rose from around the depth of 51 cm to reach peak values in the shallower depths of around 10 to 30 cm and then decreased in the top 10 cm.

4.5.2 Cu/Pb and Zn/Pb

The ratio of Cu/Pb shows a significant rise of Cu in the top 10 cm of Lake Tutaeinanga and a slight increase in Lake Ngāpouri. The values of the Zn/Pb ratio in Lake Tutaeinanga are significantly higher than all other lakes by almost a factor of 5. The ratios in Lake Ngāpouri are very high in the top 15 cm of the core compared with the rest of the core, where they are stable, while in Lake Tutaeinanga the Zn/Pb ratios are almost constant throughout the core.

In Lake Forsyth, both Cu/Pb and Zn/Pb show stable ratios in the bottom of the core up to the depth of 54 cm and then slight fluctuations in the middle of the core and finally a slight decrease in the top 15 cm of the cores. Lake

Pearson and Lake Heron show stable/constant ratios of Cu/Pb and Zn/Pb throughout the cores. In Lake Moawhitu, both ratios have relatively high values compared with other lakes and they also show that Cu and Zn are relatively high in the bottom of the core compared with the recent cores where they show almost constant ratios to Pb.

4.5.3 Molar Cd and P relationship

Molar Cd and P relationships are shown in Figure 4.12. Cd and P show similar relationships in all the lakes except in Lake Ngāpouri and Lake Forsyth. In both of these lakes, Cd and P had similar relationships in the lower and middle parts of the core, but in the top part of the core, P increased while Cd decreased.

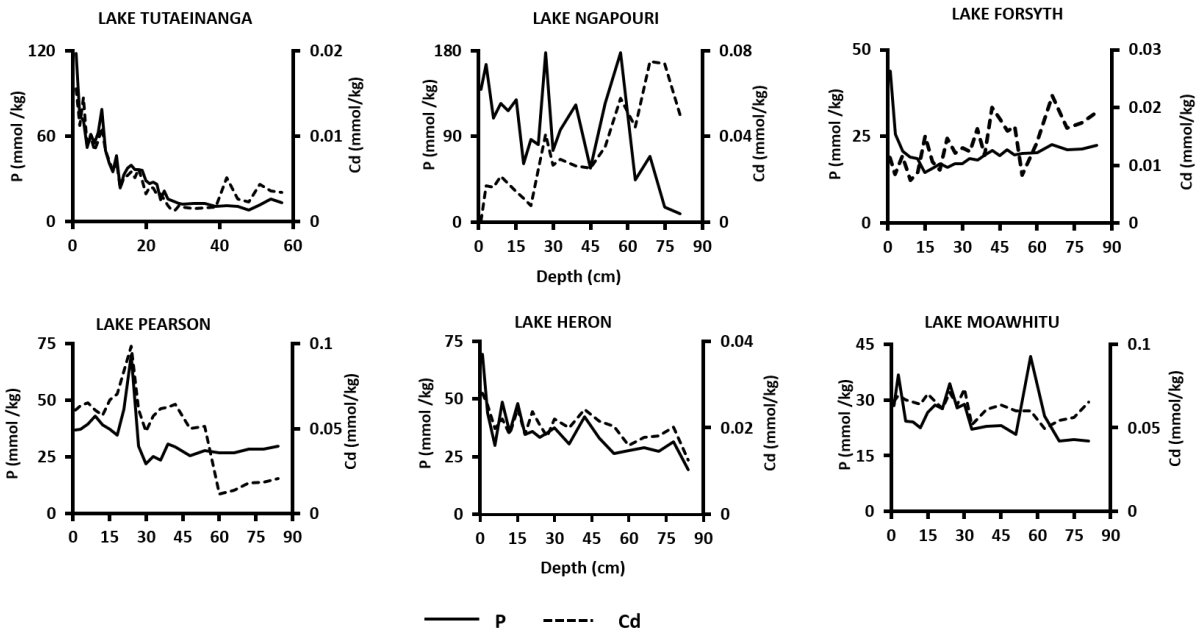

Figure 4-11 Results of relationship of Cd and P as described in Chapter 3, section 3.5.

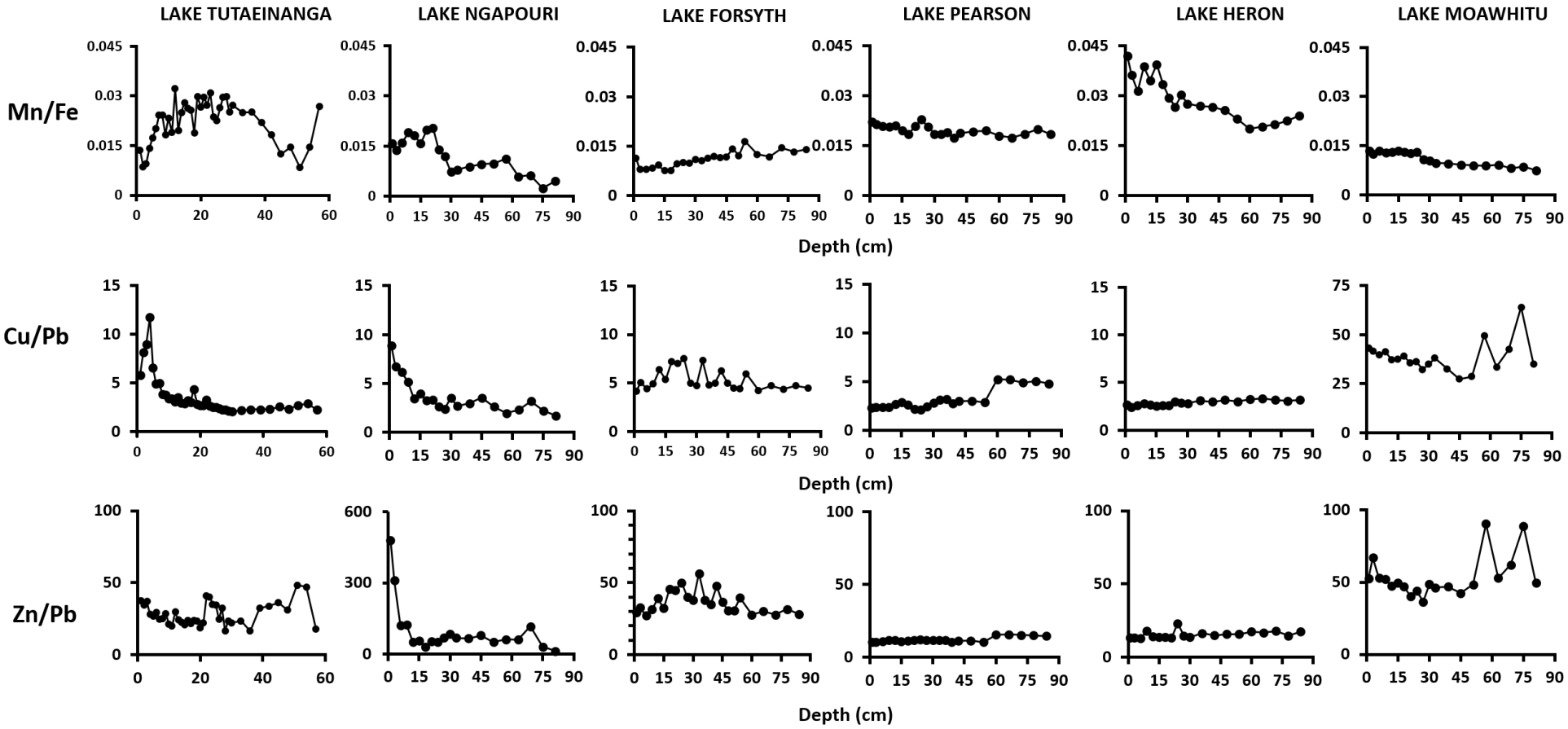

Figure 4-12 Molar ratios of Mn/Fe, Cu/Pb, Zn/Pb calculated using methods described in section 3.5. All graphs have similar scales across the line of their respective ratio except for Lake Moawhitu in the line of Cu/Pb ratio and Lake Ngāpouri in line of Zn/Pb because their values were too high and this scale would not suit the data presentation in the other graphs.

Chapter 5

Discussion

The main objective of this research was to assess whether the trace element profile in lake sediment cores can reliably identify periods of historic land use change in the catchment. Trace element trends and enrichment factors have been measured to determine whether changing land use, brought about by the arrival of Māori and then Europeans, as well as recent, more intensive use of fertilisers and other agrichemicals, has changed trace element concentrations in the lakes.

5.1 Lakes showing recent trace element enrichment

5.1.1 Lake Tutaeinanga

P showed a substantial increase in recent sediments, indicating that P-rich (generally fertilised) soils have been accumulating in the lake. Other agriculture-related trace elements should show a similar trend if they are also coming from fertilised agricultural land. In Lake Tutaeinanga, Cd showed a similar trend to P, and so did Cu (except in the most recent sediments). The EFs for Cd and Cu were also similar to that for P.

The enrichment of Cu must be mainly from anthropogenic activities associated with rural land use, rather than urban land use, as there is little urban development in this catchment. The Cu/Pb ratio in Figure 4.12 for this lake, for example, showed a rapid increase of Cu over Pb in the top 15 cm of the sediment cores, indicating a different source of copper in the near-surface sediments to that for Pb, which is a more typical contaminant from urban or road sources.

Zn and Pb concentrations showed similar trends but less enrichment (1.95 for Zn and 1.70 for Pb) and Ni also showed similar trend. Since there are no urban activities in the catchment, the source of these elements could be due to road runoff or farming activities. However, the ratio of Zn/Pb showed little change, suggesting road runoff rather than farming.

Concentrations of As in Lake Tutaeinanga are high relative to other lakes. This is because the lake is located in Taupo Volcanic Zone (TVZ), an area in the North Island known for having higher natural concentrations of As due to geothermal activities and volcanic eruptions (Robinson et al., 2004; Robinson et al., 2006). The lake is also very close to the Waiotapu geothermal area, which releases As in both cold and hot springs (Pearson, 2012). Arsenic showed the highest concentrations at the bottom of the core soon after the arrival of Māori. This period is associated with the Kaharoa volcanic eruption, that occurred around AD 1314 at Mount Tarawera, and its ash was distributed across eastern and northern parts of the North Island (Hogg et al., 2012). The EFs for Cd, As and Zn at around this period (soon after the arrival of Māori) are also relatively high. Cd, As and Zn are known to be prevalent in New Zealand volcanic ashes (Craw et al., 2005).

The Mn/Fe ratio shows Mn depletion relative to Fe in the top and base of the sediment core, relative to the middle of the core. This would be consistent with Fe oxides forming near the top of the core, and Fe sulphide in

the anoxic lower parts of the core, while Mn remains more mobile under these highly oxidising and reducing conditions respectively

The trace element results in Lake Tutaeinanga, especially those that are related to use of fertiliser (P and Cd) are consistent with current water monitoring programme indicators, which show that Lake Tutaeinanga is rich in nutrients and experiences nuisance cyanobacterial blooms. The catchment for Lake Tutaeinanga is almost 100% covered by dairy farms and partly by sheep and beef farms.

Conclusion: P, Cu and Cd show the same trends and similar enrichment, and relate to land use change, and specifically to farming (use application of fertiliser and agrichemicals in this catchment).

5.1.2 Lake Ngāpouri

P increased with time along the Lake Ngāpouri sediment core, with fluctuations, and was moderately enriched in the top 3 cm, and during the European era. However, P also showed a degree of enrichment in the Māori era. This would indicate that the enrichment of P could be coming not only from farming activities but also as a result of erosion of P-rich volcanic soils, induced by the Māori and early European settlement. The Māori settlement in New Zealand before the arrival of Europeans is associated with hunting, subsistence farming (without using fertilisers or chemicals) and burning of native vegetation to clear land for settlement or to clear thick forest to create passage (McIntyre, 2007; McWethy et al., 2010). The early settlement of Europeans is associated with clearing of native vegetation to create large commercial farms and settlement areas (McIntyre, 2007). These activities resulted in bare land which became susceptible to water or wind erosions, carrying soils derived from different parent rock material and depositing them in waterways and lakes (Molloy, 1977).

Soil erosion induced by these settlements may also be the reason for the decrease in the concentration of Cd, As and Pb with time in this lake. These elements had higher concentrations in the prehuman era and decreased in the Māori and European eras. Cu also decreased initially, but rose gradually in the European era. The soil that eroded into the lake would be from different sources (different parent materials) with low concentrations of these elements, effectively diluting the concentrations of these elements in the lake sediments.

Cd showed very low concentrations in the top part of the core compared with the base of the core (it was undetected at the depth of 1 cm). This could be associated with recent soil erosion, but may also reflect its mobility. Cd is known to be sensitive to redox reactions, whereby it becomes soluble in oxygenated conditions and precipitates immediately in anoxic condition (Al-Najjar et al., 2011; Thomson et al., 2001). Just like iron which is scavenged by sulphide ions to form iron sulphide under anoxic conditions, Cd forms cadmium sulphide. In ideal conditions, the top part of the core close to the sediment and water interface (SWI) is oxygenated while the deeper part is not oxygenated. However, Pearson (2012) made the observation in Lake Ngāpouri that the bottom waters were not oxygenated due to eutrophic conditions in the lake, and the upper sediments close to the SWI were anoxic. This may result in the eventual depletion of Cd in the top part of the core. This can also be substantiated by the values of the Mn/Fe ratio, which showed that Fe decreased in the top part of the core compared with Mn, suggesting that Fe was converted into sulphide while Mn remained mobile.

Another internal biogeochemical process that may affect the distribution of Cd in sediment cores is that Cd can be taken up by aquatic organisms found on the surface of the sediments, or in the top part of the core, and then transferred to the deeper core column in sinking organic matter (Boyle et al., 1976; Chaillou et al., 2002; Pace et al., 1987; Thomson et al., 2001)

The inconsistent variations of Cd may also be due to the fact that the determination of Cd in the soil is interfered with by the presence of arsenic (Lambkin & Alloway, 2000). Research shows that the determination of Cd by ICP-OES is affected when the concentration of arsenic is greater than 50 μg/L in the soil (Lambkin & Alloway, 2000; M. B. McBride, 2011; Waterlot & Douay, 2009).

There is an enrichment of Cu in Lake Ngāpouri, as well as a substantial enrichment of Zn, in the most recent sediments. Cu may be sourced from agricultural land (e.g., used in fungicides). Zn also shows higher concentrations in Lake Ngāpouri compared with other lakes. Pearson (2012) also found higher values of Zn (200 mg/kg) in the top part of the Lake Ngāpouri core, compared with other lakes in the TVZ. The higher concentrations and enrichment of Zn in Lake Ngāpouri could be connected to geothermal activities, the presence of Zn in superphosphate fertilisers and/or use of Zn as a remedy for facial eczema in cattle on dairy farms around the catchment (Craw et al., 2005; Kabata-Pendias, 2001; M. D. Taylor, 2011). Zn enrichment cannot be related to urban storm water because there are few urban activities in the catchment. Pb, which is an obvious indicator of urban pollution, was not enriched in Lake Ngāpouri sediments. Also the Zn:Pb ratio in Figure 4.12, showed a rapid increase of Zn over Pb in the top 15 cm of the sediment core, suggesting that Zn is coming from anthropogenic activities associated with rural land use rather than urban sources.

There are higher concentrations of As in Lake Ngāpouri than in all the other lakes studied, including nearby Lake Tutaeinanga. This could be because of Lake Ngāpouri's location in the TVZ and closer proximity to the Waiotapu geothermal area than Lake Tutaeinanga. However, the EF values show that the lake is not enriched in As in the recent sediments. This reflects the fact that the catchment is mainly covered by dairy farms where As is rarely used.

Lake Ngāpouri catchment is used intensively for agriculture with almost 100% of the area covered by dairy farms. The lake experiences frequent blooms of nuisance cyanobacteria that are caused by high concentrations of nitrogen and phosphorous from the catchment' pastoral farms and from internal P load released from the sediments during summer (Kusabs, 2017; Pearson et al., 2012).

Conclusion: Zn and Cu show enrichment in the near-surface sediments of Lake Ngāpouri, that probably relate to land use change to more intensive farming and the use of agrichemicals. P has increased slowly since the Māori era, which may be attributed to enhanced erosion of volcanic soils as land was cleared. The concentrations of other trace elements, As, Cd and Pb, appear diluted by this greater volcanic soil erosion, caused by the Māori and European settlement.

5.1.3 Lake Forsyth (Te Roto O Wairewa)

In comparison with the Lake Tutaeinanga and Lake Ngāpouri catchments, Lake Forsyth's catchment is not fully covered by agriculture. The catchment is associated with hills and steep slopes, which are not conducive for several farm activities, and it includes the town of Little River and a major road running alongside the lake.

Zn, Cu and Pb all showed increasing concentrations in the top 30 cm of the core, and relatively high concentrations in prehuman times, suggesting there has been dilution by volcanic soil erosion in the catchment, as observed in Lake Ngāpouri. Other trace elements (Fe, Mn, Al, Cr, Ni and V) showed similar trends that suggest soil erosion in the catchment. The elements had high concentrations in the prehuman era, which decreased through the Māori and European eras, suggesting that new soils from the catchment with lower concentrations of the trace elements than the existing concentrations eroded into the lake. Several authors have also reported that rapid deforestation and destruction of native forest through bush fires caused excessive erosion that led to severe and rapid sedimentation in the lake (Eric, 1992; Flint, 2007; Lynn, 2005; Main, 2002; McIntyre, 2007).

The EFs for Cu, Pb and Zn in Lake Forsyth are all similar and *slightly polluted* in the top part of the core, suggesting a common, recent source. Cu-Pb-Zn is an association commonly found in road runoff and urban storm waters, and this suggests that poor water quality in Lake Forsyth may not be due to input of fertilisers, volcanic soils and agrichemicals alone but also from lifestyle blocks in the area and road runoff. Some of the Cu may be linked to use of copper as a fungicide in the viticulture blocks. However, the ratios for Cu/Pb and Zn/Pb show that Pb is slightly higher in the top 20 cm of the core, suggesting a predominantly urban influence or road runoff.

P showed a rapid increase in recent sediments, as did Cd in the two previously collected cores (F10 and F11), but not in the Lakes380 core collected for this study. P is slightly enriched in Lake Forsyth, meaning higher nutrients in the lake may not be from fertiliser or human influence only. The P trends are consistent with past studies, which showed that the current hypertrophic state of Lake Forsyth is not only a result of input of fertilisers or agrichemicals from agriculture land use, but also from the lake's bedrock (basaltic rock) and the soils derived from the surrounding catchment, which have higher natural concentrations of P (Eric, 1992; Lynn, 2005). Eric (1992) reported that the fertilisers that were used between the 1960s and 1980s in dairy, sheep and beef farms in the Lake Forsyth catchment and in the neighbouring valleys were not significant enough to cause the hypertrophic status of the lake.

Cd concentrations in the main core for this study decreased with time, but in cores taken at F11 and F10 (Figures 3.9 and 4.12), Cd concentrations were stable throughout the core except in the top 1 cm where they rose abruptly. Also the F10 core showed higher concentrations than the main core and the F11 core. The inconsistency of Cd profiles within one lake could be associated with the uneven distribution of recent sediments in the lake.

As is also slightly enriched in Lake Forsyth. The slight enrichment may be linked to the use of pesticides in sheep dips, or perhaps to a higher concentration in volcanic soils.

Conclusion: The trends for most trace elements and P are mainly affected by the erosion of volcanic soils in the catchment, after European and Māori arrival and associated land clearance than application of fertilisers and

agrichemicals. Zn, Cu and Pb all have similar trends and enrichment factors suggesting an urban storm water or road runoff origin, as well as dilution by soil erosion. The trend of Cd and P reflect soil erosion in the catchment during the Māori and European eras, but also very recent enrichment in the near-surface sediments.

5.2 Lakes lacking significant recent trace element enrichment

5.2.1 Lake Pearson

Most trace elements in Lake Pearson showed inconsistent trends and did not show significant enrichments. P, As and Cd were slightly enriched while Cu, Zn and Pb were not enriched in recent sediments. These findings might be reflecting that the catchment has been partially used for agriculture land use activities. History shows that the catchment for this lake has been mainly used for sheep farming since the arrival of Europeans in around the 1850s (Molloy, 1977), and sheep farming is known to use less fertilisers than dairy farming. Also, Lake Pearson has a relatively small area of the catchment that is used for agriculture compared with other lakes studied. The current water quality monitoring programme for Lake Pearson also shows *average* or *good* conditions. The TLI for Lake Pearson for the past 15 years has either been level 2–3 (oligotrophic) which means *good* conditions or level 3–4 (mesotrophic) which means *average* conditions (LAWA, 2017a). Lake Pearson has had high ecological health with an average SPI of 55% for the past 10 years (LAWA, 2017a). Therefore, this implies that the lake catchment did not experience significant agricultural land use changes or major inputs from agricultural land uses.

Cd and P in this lake showed similar trends, especially in the top part of the core in the Māori and European eras where they showed slight enrichment. The slight enrichment of Cd and P could be linked to the use of fertilisers in sheep farming in the catchment. Also, the enrichment of these elements in the Māori era could possibly be indicating soil erosion into the lake caused by the Māori settlement and land use activities.

The slight enrichment of As could be linked to the use of As in pesticides in sheep dips. There is no literature or evidence of the other uses of As in the catchments of the three lakes. Also, sheep dips are usually on a small scale and can easily be controlled (as a point source pollution) and cause perhaps only a slight enrichment.

Cu, Zn and Pb are not enriched in this lake and both the Zn/Pb ratio and Cu/Pb ratios are constant, suggesting zero urban activities in the catchment and little contribution from road runoff. It is perhaps surprising considering the proximity of Lake Pearson to State Highway 73.

Conclusion: P, Cd and As have similar slight enrichment, while Cu, Zn and Pb are not enriched, in the recent sediments in Lake Pearson. These could be indicating that the lake catchment did not experience significant agricultural land use changes. The results agree with the current water monitoring programme which shows *average* to *good* water quality conditions for the lake over the past 15 years.

5.2.2 Lake Heron

P increased in the top 6 cm of the core, indicating very recent accumulation of P-rich soils in the lake. Cd and As also showed similar trend to P, and all the agriculturally related trace elements have similar slight enrichment

except for Zn, which is not enriched. These findings also reflect the current water conditions in Lake Heron. The current water monitoring programme shows that the water quality in the past 40 years has either been in *average* or *good* state (LAWA, 2017a), as for Lake Pearson. The TLI for both lakes for the past 15 years have either been level 2–3 (oligotrophic) which means *good* conditions, or level 3–4 (mesotrophic) which means *average* conditions (LAWA, 2017a). Lake Heron has had moderate ecological health, with an average SPI of 45% for the past 40 years (LAWA, 2017a). The slight pollution in the catchment could be because it has been partially used for agriculture activities, and mainly covered by sheep and beef farming that use less fertilisers and irrigation than dairy farming.

The enrichment factors for all the agriculture-related trace elements showed a similar trend in the Māori era, all rising gradually. This could be linked to soil erosion and increased sedimentation due to the land use activities associated with the Māori settlement. The soil erosion brought in new sediments with higher concentrations than the existing sediments.

The Mn/Fe ratio in Lake Heron show that Mn increased while Fe decreased in the upper part of the core. This would be consistent with Fe oxides forming near the top of the core. Both the Cu/Pb and Zn/Pb ratios are constant throughout the cores, suggesting undisturbed conditions of these elements or similar natural source of the elements.

Conclusion: Cd, P and As showed similar trends in Lake Heron, but only minor enrichment. All the agriculture-related trace elements showed similar increasing trends and enrichment factors in the Māori era, suggestive of enhanced soil erosion beginning in this era.

5.2.3 Lake Moawhitu

P, Cd, Zn, Cu and Pb showed similar trends in concentrations along the sediment core, with P, Cu and Zn being slightly enriched in the very top of the Lake Moawhitu sediment core, and Cd and As not enriched in any part of the sediment core. Just like in Lake Forsyth, these results may reflect minor rural land use activities in the catchment but are not reflected in the water quality in the lake itself, which is super-trophic.

History shows that Lake Moawhitu has had beef farm activities but it has not been used intensively. In 2004, the farm activities in the catchment were replaced after the catchment was purchased by the Nature Heritage fund and passed to Department of Conservation (DOC) (Kelly et al., 2019). Currently the catchment is mainly covered by high-producing exotic grassland and native vegetation.

Lake Moawhitu is super-trophic, however, and experiences frequent algal blooms. The concentrations of total P load and total N load are higher than the New Zealand national guidelines for protection of aquatic life at all sampling points (Kelly et al., 2019). The poor water quality in this lake cannot be the result of inputs from fertilisers and agrichemicals only. Kelly et al. (2019) reported that there were very high levels of nutrients in the lake compared with the surrounding inflowing streams and other tributaries, suggesting that internal nutrient cycling is the major source of nutrients in Lake Moawhitu than from surrounding agriculture inputs. Also, the higher P load in the lake might be coming from the surrounding catchment soils, considering that the lithology

of the catchment is dominated by basaltic volcanic rocks. Therefore, P in the lake is not from fertiliser input only, and so Cd may not be expected to be enriched in the lake.

The Mn/Fe ratio in Lake Moawhitu shows a slight rise of Fe over Mn, indicating a possible reducing environment in the top core. This would also cause depletion of Cd in the top core as Cd is scavenged by sulphate in the reducing environment.

The enrichment factors of P, Cd, Cu and Zn soon after the beginning of the Māori era are higher, suggesting soil erosion into the lake, caused by the Māori settlement land use activities. The Māori of Ngāti Koata and a hapū of Ngāti Toa tribes are believed to have settled in the catchment and used the lake as a source of mahinga kai (food) (Kelly et al., 2019). The settlement of the Māori are associated with the burning of the native vegetation to aid hunting and create settlement areas and passages (McIntyre, 2002).

Conclusion: P, Zn and Cu have shown similar EFs that may relate to the rural land use change in the Lake Moawhitu catchment, but these trace element show very little recent enrichment.

5.3 The best trace element indicators for land use change in farming catchments

5.3.1 European era (recent sediments)

The trends with time and enrichment factors of the best trace element indicators need to relate directly to rural land use changes in the catchment. P has shown consistency in indicating recent P-rich soil input in all the lakes studied. In lowland lakes (Lake Ngāpouri and Lake Tutaeinanga) where the land has been intensively used for dairy farming, P showed substantial enrichment in recent cores. In highland lakes (Lake Pearson and Lake Heron) where the catchment has been partly used for agriculture, P was only slightly or not enriched. The slight enrichment in highland lakes was consistent with the current water monitoring programmes, which indicate that the water quality in these lakes are in *good* condition.

In coastal lakes (Lake Forsyth and Lake Moawhitu) where the catchments have also been partially used for agriculture, P showed slight or no enrichment in young sediments in the cores. The slight enrichments in coastal lakes are not consistent with the water quality of the lakes, which have supertrophic conditions. However literature has shown that higher levels of nutrients in these lakes are not only from agriculture inputs but also from natural basaltic P-rich soils and internal nutrients cycling.

Since P enrichment in recent sediments provides a good indication of P-rich soils getting into a lake, the agriculture-related trace elements should show a similar trend if they are also coming from fertilised agricultural land. Cu and Zn have shown similar enrichment to P across the lakes, indicating their enrichment is from agricultural land use activities.

Cd showed similar enrichment to P in Lake Tutaeinanga, Lake Pearson and Lake Heron, but not in the supertrophic Lakes Ngāpouri and Moawhitu, and enrichment was patchy in Lake Forsyth. Cd concentration or enrichment in the highly eutrophic lakes was often higher at the bottom of the cores compared with the younger sediments.

This could be due to biogeochemical processes in eutrophic lakes (Boyle et al., 1976; Pearson, 2012; Thomson et al., 2001), but could also be due to the erosion of P-rich volcanic soils that contain low concentrations of Cd compared with P from fertiliser inputs (McLaughlin & Singh, 1999).

Arsenic showed similar enrichment to P in Lake Forsyth, Pearson and Heron, which have catchments that are mainly covered with sheep and beef farms, where As could potentially be used as pesticide in sheep dips. Arsenic was not related to P enrichment in Lake Moawhitu, Lake Ngāpouri and Lake Tutaeinanga. This could be due to As inputs from volcanic and geothermal activities prevalent in the catchment. Also these catchments have been mainly covered by cattle farms which do not typically use As, unlike horticultural farms and sheep dips.

Conclusion: P, Cu and Zn have shown consistency in indicating recent rural land use changes in the lakes studied. Cd can be used as indicator or rural land use change but with more understanding of the factors that affect the biogeochemical process of Cd in eutrophic lakes. Arsenic can also be used as an indicator of rural land use as long as the catchment is not affected by volcanic and geothermal activities.

5.3.2 Māori Land use activities (early settlement)

The best way of understanding the impact of the early settlement of Māori on the enrichment of trace elements in lakes is by looking at the trends of concentrations or enrichment of the elements through that earlier era. Constant concentrations would mean undisturbed conditions while rising or decreasing concentration trends would mean impacts from the Māori land use. The land use activities that are associated with the Māori settlement in New Zealand before the arrival of Europeans are hunting, subsistence farming (without using fertilisers or chemicals) and burning of native vegetation to clear land for settlement or to clear thick forest to create path for them to move from one place to another (McIntyre, 2007; McWethy et al., 2010). These activities would have resulted in bare land that became susceptible to water or wind erosion, carrying sediments of different parent materials and depositing them in waterways and lakes (Molloy, 1977). This could result in the rise or fall of the concentration of trace elements in the sediments after the arrival of Māori, depending on the parent materials from which the sediment originated.

In Lake Tutaeinanga, concentrations of Cd, As and Zn after the arrival of Māori decreased, suggesting potential erosion of sediments with lower concentrations into the lake. In Lake Heron, enrichment of Cd, As, Cu, P, Pb and Zn after the arrival of Māori increased, suggesting potential erosion of sediments, with higher concentrations getting into the lake as a result of Māori settlement. The slightly enriched P, Cd and As in the Māori era in Lake Moawhitu, Pearson and Ngāpouri would also point to a similar cause.

Conclusion: Depending on the lithology of the catchment area, any of the studied trace elements can be used as indicators of enhanced catchment soil erosion, as might have occurred during Māori settlement. Their impact can be traced by looking at the trends of the concentrations or enrichment in the cores, and relating this to parent rock geology.

Chapter 6: Conclusion and Recommendation

6.1 Conclusion

The main aim of this study was to assess the potential of using trace element signatures in lake sediment cores, as indicators of rural land use change. Sediment cores were collected from six New Zealand lakes situated in various agricultural land use settings: two lowland lakes (Lake Tutaeinanga and Lake Ngāpouri), two coastal lakes (Lake Moawhitu and Lake Forsyth/Wairewa) and two highland lakes (Lake Pearson and Lake Heron). With help from the Lakes380 project, four cores were taken per lake and one core was split along the middle. One half was subsampled, and the other half scanned using a hyperspectral scanner and an ITRAX XRF scanner at University of Otago. The remaining cores were stored by freezing them in total darkness for future analysis. The subsampled cores were dated and analysed for geochemical markers.

Given that it is very expensive to date sediments using radiometric methods, this research relied on pollen analysis to identify the prehuman era and major human settlement periods (Māori and European settlements). The pollen analysis targeted the presence of exotic taxa such as sorrel (Rumex), willow (Salix), and pine (Pinus) as well as fern content to indicate changes of vegetation that came after the arrival of Europeans, and charcoal to indicate the arrival and vegetation changes caused by Māori.

For trace element analysis the sediment cores were subsampled at intervals of 3 cm in the post-European era and at interval of 6 cm in the pre-European period. Then the subsamples were digested and analysed using inductively coupled plasma – optical emission spectrometry (ICP-OES) analysis at Lincoln University to determine trace element concentrations. The trace elements targeted were those that are commonly used in New Zealand agriculture (As, Cd, Cu, P, and Zn), and other trace elements that may provide supporting information on the agriculturally relevant trace element sources and distribution.

The research also determined enrichment factors to differentiate trace elements originating from anthropogenic activities and those from prehuman conditions. The trace element concentrations and enrichments were linked to the history of land use changes in the respective lake's catchments, to assess whether the trace element profile in the lake sediment cores identified periods of historic land use change in the catchment.

The results of the study showed trends in concentrations and enrichment factors that could indicate changing land use – brought about by the arrival of Māori and then Europeans, as well as recent more intensive use of fertilisers and other agrichemicals – which has changed trace element concentrations in the lake.

The trends in concentrations and enrichment of trace elements in sediments deposited during the Māori era have signalled potential impacts of the Māori settlement in the catchments of the lakes studied. For instance, in Lake Tutaeinanga, the concentrations of Cd, As and Zn decreased after the arrival of Māori, suggesting potential erosion of soils from a different parent rock material, reducing trace element concentrations getting into the lake. In Lake Heron the apparent slight enrichment of Cd, As, Cu, P, Pb and Zn during the Māori era suggests potential erosion of sediments from a different parent material, with higher concentrations of these elements,

entering the lake. The Māori settlement era is associated with land use activities such as hunting, subsistence farming (without using fertilisers or chemicals) and burning of native vegetation to clear passages or settlement areas. This led to bare land which became susceptible to soil erosion.

In the more recent European era, P showed significant enrichment in catchments of lowland lakes that have been intensively used for dairy farming and slight (less significant) enrichment in catchments of both coastal and highland lakes that have been partially used for agriculture. Since P enrichment in recent sediments provides a good indication of P-rich (generally fertilised) soils getting into the lake, the agriculture-related trace elements should show a similar trend if they are also coming from fertilised agricultural land. Cu and Zn showed similar enrichment to P across the lakes. Cd enrichment in eutrophic lakes may have been affected by biogeochemical processes in eutrophic lakes. Arsenic showed similar enrichment to P, Cu and Zn in Lake Forsyth, Lake Pearson and Lake Heron. The distribution of As in Lake Tutaeinanga and Lake Ngāpouri is affected by volcanic and geothermal activities prevalent in the catchment.

Studies of the trace elements have therefore shown that some can be used as indicators of long-term rural land use change, but they need to be used in the context of catchment erosion and lake biogeochemical processes. Arsenic can be used as an indicator of rural land use as long as the catchment is not affected by volcanic and geothermal activities. Cd can also be used as an indicator of rural land use change, but more understanding of the factors that affect its biogeochemical processes in eutrophic lakes is required.

6.2 Management implications and Recommendations for further research

The following are some of the implications the results of this research may have for water resource management in New Zealand;

- The research has shown enrichment of some elements in both Maori and European eras that suggested that soil erosion was caused by activities associated with both eras. Therefore, management measures should be taken to control further soil erosion, which might cause further soil accumulation of these elements.

- The agriculturally-related trace elements are more enriched in low-lying areas and coastal areas compared to highland areas which have experienced recent agricultural land use change. This could imply that more emphasis to control further enrichment of elements, should be given to those low-lying areas. However, recent slight enrichment of these elements in highland areas which have experienced recent agriculture land use development implies that emphasis should also be given to highland areas to ensure that control prevents more damage.

Some of the limitations of this research provide the basis for recommendations for future research on this topic.

- This study used pollen analysis methods to determine prehuman era and major human settlement periods. Radiometric dating methods are preferred, as they provide more detailed dates that would even help to identify periods of intensive land use. However, it is very expensive to date sediments using

radiometric methods; this technique was being used by the Lakes380 project for some of the lakes in this study but the results were not available within the timeframe of this study.

- The lakes studied did not include lakes with catchments dominated by horticultural farms where Cu, Zn and As may be used. At the time when this research started, the Lakes380 project had not yet collected or planned to collect cores from lakes with catchments that are dominated by horticultural farms.

- There was insufficient time to study the behaviour of trace elements (commonly used in agricultural land activities) within lake sediment cores or the biogeochemical dynamics that influence the mobility or distribution of these trace elements in the cores. Such studies need to be carried out to help establish the factors that influence the concentrations of trace elements in these lake sediment cores.

- More sediment cores from each lake may be needed to provide a more representative assessment of past lake conditions. In Lake Forsyth/Wairewa for example, three cores were used in this study and showed differences in Cd trace element distributions that may relate to sediment deposition and erosion regimes within the lake.

References

Abbott, M. B., Wolfe, B. B., Wolfe, A. P., Seltzer, G. O., Aravena, R., Mark, B. G., . . . Vuille, M. (2003). Holocene paleohydrology and glacial history of the central Andes using multiproxy lake sediment studies. *Palaeogeography, Palaeoclimatology, Palaeoecology, 194*(1), 123-138. doi:https://doi.org/10.1016/S0031-0182(03)00274-8

Abrahim, G., & Parker, R. (2002). Heavy-metal contaminants in Tamaki Estuary: impact of city development and growth, Auckland, New Zealand. *Environmental Geology, 42*(8), 883-890.

Acevedo-Figueroa, D., Jiménez, B., & Rodríguez-Sierra, C. (2006). Trace metals in sediments of two estuarine lagoons from Puerto Rico. *Environmental Pollution, 141*(2), 336-342.

Adriano, D. C. (1986). *Trace elements in the terrestrial environment*. Berlin: Springer-Verlag.

Afzal, M., Yu, M., Tang, C., Zhang, L., Muhammad, N., Zhao, H., . . . Xu, J. (2019). The negative impact of cadmium on nitrogen transformation processes in a paddy soil is greater under non-flooding than flooding conditions. *Environment International, 129*, 451-460. doi:10.1016/j.envint.2019.05.058

Agency for Toxic Substances and Disease Registry (ATSDR). (2014). Public Health Studies from Agency for Toxic Substances and Disease Registry Further Understanding of Public Health (Implementing Systematic Review in Toxicological Profiles: ATSDR and NIEHS/NTP Collaboration). In (pp. 482). Atlanta.

Aggett, J., & Kriegman, M. R. (1988). The extent of formation of arsenic(III) in sediment interstitial waters and its release to hypolimnetic waters in Lake Ohakuri. *Water Research, 22*(4), 407-411. doi:10.1016/0043-1354(88)90034-6

Al-Khashman, O. (2009). Chemical Evaluation of Ma'an Sewage Effluents and its Reuse in Irrigation Purposes. *Water Resources Management, 23*(6), 1041-1053. doi:10.1007/s11269-008-9313-1

Al-Najjar, T., Rasheed, M., Ababneh, Z., Ababneh, A., & Al-Omarey, H. (2011). Heavy metals pollution in sediment cores from the Gulf of Aqaba, Red Sea. *Natural science, 3*(09), 775.

Alkarkhi, A., Ahmad, A., & Easa, A. (2008). Assessment of surface water quality of selected estuaries of Malaysia: Multivariate statistical techniques. *Environmentalist, 29*, 255-262. doi:10.1007/s10669-008-9190-4

Alloway, B. J. (1990). *Heavy metals in soils*. Glasgow : New York: Glasgow : Blackie,New York : Halsted Press.

Alloway, B. J. (2013). *Heavy Metals in Soils: Trace Metals and Metalloids in Soils and their Bioavailability* (Vol. 22). Dordrecht: Springer Netherlands, Dordrecht.

Almeida, C., Quintar, S., González, P., & Mallea, M. (2007). Influence of urbanization and tourist activities on the water quality of the Potrero de los Funes River (San Luis – Argentina). *An International Journal Devoted to Progress in the Use of Monitoring Data in Assessing Environmental Risks to Man and the Environment, 133*(1-3), 459-465. doi:10.1007/s10661-006-9600-3

Amber, D. (2006). *Pasture, present and future – A brief history of pastoralism in New Zealand*. New Zealand Minstry of Agriculture and Forest

Amin, B., Ismail, A., Arshad, A., Yap, C. K., & Kamarudin, M. S. (2009). Anthropogenic impacts on heavy metal concentrations in the coastal sediments of Dumai, Indonesia. *Environmental monitoring and assessment, 148*(1-4), 291-305.

Augustinus, P., Reid, M., Andersson, S., Deng, Y., & Horrocks, M. (2006). Biological and Geochemical Record of Anthropogenic Impacts in Recent Sediments from Lake Pupuke, Auckland City, New Zealand. *Journal of Paleolimnology, 35*(4), 789-805. doi:10.1007/s10933-005-5306-8

Beer, J., & Sturm, M. (1995). DATING OF LAKE AND LOESS SEDIMENTS. *Radiocarbon, 37*(1), 81-86.

Berthelsen, B., Steinnes, E., Solberg, W., & Jingsen, L. (1995). Heavy metal concentrations in plants in relation to atmospheric heavy metal deposition. *Journal of Environmental Quality, 24*(5), 1018-1026.

Bing, H., Wu, Y., Liu, E., & Yang, X. (2013). Assessment of heavy metal enrichment and its human impact in lacustrine sediments from four lakes in the mid-low reaches of the Yangtze River,

China. *Journal of Environmental Sciences, 25*(7), 1300-1309. doi:10.1016/S1001-0742(12)60195-8
Bolan, N., Adriano, D., & Mahimairaja, S. (2004). Distribution and Bioavailability of Trace Elements in Livestock and Poultry Manure By-Products. *Critical Reviews in Environmental Science and Technology, 34*(3), 291-338. doi:10.1080/10643380490434128
Bolan, N., & Thiagarajan, S. (2001). Retention and plant availability of chromium in soils as affected by lime and organic matter amendments. *Soil Research, 39*, 1091-1103. doi:10.1071/SR00090
Boller, M. A., & Steiner, M. (2002). Diffuse emission and control of copper in urban surface runoff. *Water science and technology : a journal of the International Association on Water Pollution Research, 46*(6-7), 173. doi:10.2166/wst.2002.0677
Boyle, E. A., Sclater, F., & Edmond, J. (1976). On the marine geochemistry of cadmium. *Nature, 263*(5572), 42-44.
Brady, J. P., Ayoko, G. A., Martens, W. N., & Goonetilleke, A. (2015). Development of a hybrid pollution index for heavy metals in marine and estuarine sediments. *Environmental monitoring and assessment, 187*(5), 306.
Broadley, M. R., White, P. J., Hammond, J. P., Zelko, I., & Lux, A. (2007). Zinc in plants. *New phytologist, 173*(4), 677-702.
Bruland, K. W., Knauer, G. A., & Martin, J. H. (1978). Cadmium in northeast Pacific waters 1. *Limnology and Oceanography, 23*(4), 618-625.
Burrows, C. (1977). Cass: history and science in the Cass district, Canterbury, New Zealand. *Department of Botany, University of Canterbury, Christchurch*.
Burt, T. P., Heathwaite, A. L., & Trudgill, S. T. (1993). *Nitrate: processes, patterns and management*: John Wiley & Sons.
Buylaert, J. P., Jain, M., Murray, A. S., Thomsen, K. J., Thiel, C., & Sohbati, R. (2012). A robust feldspar luminescence dating method for Middle and Late P leistocene sediments. *Boreas, 41*(3), 435-451.
Cambridge Dictionary. (2008). Cambridge online dictionary. Retrieved from https://dictionary.cambridge.org/dictionary/english/urbanization
Canterbury Maps. (2014). Asurequality Agribase Farm Boundaries; Boundaries for farms registerd with Asurequality's Agribase system. *Canterbury Maps.* Retrieved from https://opendata.canterburymaps.govt.nz/datasets/b6e21eb7716742e7be1229c6e1f8d0ad
Chaillou, G., Anschutz, P., Lavaux, G., Schäfer, J., & Blanc, G. (2002). The distribution of Mo, U, and Cd in relation to major redox species in muddy sediments of the Bay of Biscay. *Marine Chemistry, 80*(1), 41-59.
Chaney, R. L., Ryan, J. A., Li, Y., & Brown, S. L. (1999). *Soil cadmium as a threat to human health*. Dordrecht, The Netherlands: Cadmium in Soils and Plants. Kluwer Academic Publishers.
Chattopadhyaya, M. C., Soares, M. G., Campos, M. T. d. J. S., Ismadji, S., Lofrano, G., Barakat, M., . . . Sharma, S. K. (2014). *Heavy metals in water: presence, removal and safety*: Royal Society of Chemistry.
Chen, Y., Wang, C., & Wang, Z. (2005). Residues and source identification of persistent organic pollutants in farmland soils irrigated by effluents from biological treatment plants. *Environment International, 31*(6), 778-783. doi:10.1016/j.envint.2005.05.024
Cheng, M., Wu, L., Huang, Y., Luo, Y., & Christie, P. (2014). Total concentrations of heavy metals and occurrence of antibiotics in sewage sludges from cities throughout China. *Total concentrations of heavy metals and occurrence of antibiotics in sewage sludges from cities throughout China, 14*(6), 1123-1135.
Chirenje, T., Ma, L., Szulczewski, M., Littell, R., Portier, K., & Zillioux, E. (2003). Arsenic Distribution in Florida Urban Soils. *Journal of Environmental Quality - J ENVIRON QUAL, 32*. doi:10.2134/jeq2003.0109
Chittenden, E., Childs, C., & Smidt, R. (1976). Sediments of Lakes Rotoroa and Rotoiti, South Island, New Zealand. *New Zealand journal of marine and freshwater research, 10*(1), 61-76.
Cichota, R., & Snow, V. O. (2009). Estimating nutrient loss to waterways-an overview of models of relevance to New Zealand pastoral farms. *New Zealand Journal of Agricultural Research, 52*(3), 239-260. doi:10.1080/00288230909510509

Cohen, A. S. (2003). *Paleolimnology: The History and Evolution of Lake Systems*: United States: Oxford University Press.
Councell, T. B., Duckenfield, K. U., Landa, E. R., & Callender, E. (2004). Tire-wear particles as a source of zinc to the environment. *Environmental science & technology, 38*(15), 4206-4214.
Craw, D., Brown, K., & Webster-Brown, J. (2005). Metals derived from gold mining and geothermal sources. *Metal Contaminants in New Zealand. Resolutionz Press, Christchurch*, 231-246.
Cromarty, P. (1996). *A directory of wetlands in New Zealand*. Wellington, N.Z.: Wellington, N.Z. : Dept. of Conservation.
DairyNZ. (2019). QuickStats about dairying –WAIKATO REGION. Retrieved from https://www.dairynz.co.nz/media/5792403/quickstats-about-dairying-waikato-2019-v2.pdf
David, G. (2008). Southland region: Farming: 1950s to present day. Retrieved from http://www.TeAra.govt.nz/en/southland-region/page-8
Davis, A. P., Traver, R. G., & Hunt, W. F. (2010). Improving Urban Stormwater Quality: Applying Fundamental Principles. *Journal of Contemporary Water Research & Education, 146*(1), 3-10. doi:10.1111/j.1936-704X.2010.00387.x
Dawson, T. E., Siegwolf, R. T. W., & Siegwolf, R. (2007). *Stable Isotopes as Indicators of Ecological Change* (Vol. 1): Elsevier Science.
de Baar, H. J., Saager, P. M., Nolting, R. F., & van der Meer, J. (1994). Cadmium versus phosphate in the world ocean. *Marine Chemistry, 46*(3), 261-281.
Du Laing, G., Rinklebe, J., Vandecasteele, B., Meers, E., & Tack, F. (2008). Trace Metal Behaviour in Estuarine and Riverine Floodplain Soils and Sediments: A Review. *The Science of the total environment, 407*, 3972-3985. doi:10.1016/j.scitotenv.2008.07.025
Duinker, J., Hillebrand, M. T. J., Nolting, R., & Wellershaus, S. (1982). The river Elbe: processes affecting the behaviour of metals and organochlorines during estuarine mixing. *Netherlands Journal of Sea Research, 15*(2), 141-169.
Ekoa Bessa, A. Z., Ngueutchoua, G., & Ndjigui, P. D. (2018). Mineralogy and geochemistry of sediments from Simbock Lake, Yaoundé area (southern Cameroon): provenance and environmental implications. *Arabian journal of geosciences, 11*(22), 1-18. doi:10.1007/s12517-018-4061-x
Elliott, S. (2002). *Land-water interactions*. Wellington, N.Z.: Wellington, N.Z. : Ministry for the Environment.
Eric, P. (1992). *Sustainable water management: an approach based on the Gaia hypothesis and the traditional Maori worldview.* Lincoln University,
FAO. (2017). *Water pollution from agriculture: a global review*. Retrieved from Rome:
Fishingmag. (2015). Lake Pearson – Easy access from the nearby highway for trout fishing. Retrieved from https://fishingmag.co.nz/canterbury
Flint, E. A. (2007). *Wairewa-Lake Forsyth (Canterbury) and its blooms of Nodularia spumigena Mert* Retrieved from Lincoln:
Forstner, U., & Wittmann, G. (1979). Metal pollution in the Aquatic Environment. *Journal of Basic Microbiology, 21*(7), 38-41.
Foy, R., RH, F., RV, S., RJ, S., & DA, S. (1982). Identification of factors affecting nitrogen and phosphorus loadings to Lough Neagh.
Frignani, M., & Bellucci, L. (2004). Heavy Metals in Marine Coastal Sediments: Assessing Sources, Fluxes, History and Trends. *Annali di chimica, 94*, 479-486. doi:10.1002/adic.200490061
Gendron, A., Silverberg, N., Sundby, B., & Lebel, J. (1986). Early diagenesis of cadmium and cobalt in sediments of the Laurentian Trough. *Geochimica et Cosmochimica Acta, 50*(5), 741-747.
Gillispie, E., Sowers, T., Duckworth, O., & Polizzotto, M. (2015). Soil Pollution Due to Irrigation with Arsenic-Contaminated Groundwater: Current State of Science. *Current Pollution Reports, 1*(1), 1-12. doi:10.1007/s40726-015-0001-5
Glasby, G. (1975). *Geochemistry of superficial lake sediments from the South Island, New Zealand*: New Zealand Oceanographic Institute.
Gobeil, C., Silverberg, N., Sundby, B., & Cossa, D. (1987). Cadmium diagenesis in Laurentian Trough sediments. *Geochimica et Cosmochimica Acta, 51*(3), 589-596.

Google Maps. (2020a). Lake Heron Retrieved from https://www.google.com/maps/place/Lake+Heron
Google Maps. (2020b). Lake Ngapouri and Lake Tutaeinanga Retrieved from https://www.google.com/maps/search/Lake+Ngapouri+and+lake+Tutaeinanga
Gudasz, C., Bastviken, D., Steger, K., Premke, K., Sobek, S., & Tranvik, L. J. (2010). Temperature-controlled organic carbon mineralization in lake sediments. *Nature, 466*(7305), 478-481. doi:10.1038/nature09186
Gunawardena, J., Egodawatta, P., Ayoko, G. A., & Goonetilleke, A. (2013). Atmospheric deposition as a source of heavy metals in urban stormwater. *Atmospheric Environment, 68*, 235-242.
Hajdas, I., Ivyochs, S. D., & Bonani, G. (1995). PROBLEMS IN THE EXTENSION OF THE RADIOCARBON CALIBRATION CURVE (10-13 KYR BP). *Radiocarbon, 37*(1), 75-79.
Hogg, A., Lowe, D. J., Palmer, J., Boswijk, G., & Ramsey, C. B. (2012). Revised calendar date for the Taupo eruption derived by 14C wiggle-matching using a New Zealand kauri 14C calibration data set. *The Holocene, 22*(4), 439-449. doi:10.1177/0959683611425551
Holz, G. (2004). Dairy: healthy food from a healthy environment. *Australian Journal of Dairy Technology, 59*(2), 90-94.
Huang, K.-M., & Lin, S. (2003). Consequences and implication of heavy metal spatial variations in sediments of the Keelung River drainage basin, Taiwan. *Chemosphere, 53*(9), 1113-1121.
Ioannides, K., Ioannides, K., Stamoulis, K., Stamoulis, K., Papachristodoulou, C., Papachristodoulou, C., . . . Tsodoulos, I. (2015). Distribution of heavy metals in sediment cores of Lake Pamvotis (Greece): a pollution and potential risk assessment. *Environ Monit Assess, 187*(1), 1-16. doi:10.1007/s10661-014-4209-4
Irwin, J. (1971). Exploratory limnological studies of Lake Manapouri, South Island, New Zealand. *New Zealand journal of marine and freshwater research, 5*(1), 164-177.
Irwin, J. (1972). Sediments of Lake Pukaki, South Island, New Zealand. *New Zealand journal of marine and freshwater research, 6*(4), 482-491.
Irwin, J. (1978). Bottom sediments of Lake Tekapo compared with adjacent Lakes Pukaki and Ohau, South Island, New Zealand. *New Zealand journal of marine and freshwater research, 12*(3), 245-250.
Jellyman, D. J. (2007). *The status of eel stocks in Wairewa (Lake Forsyth)*. Wellington [N.Z.]: Wellington N.Z. : Ministry of Fisheries.
John, W. (2006a). Canterbury region - Agriculture after 1900. Retrieved from http://www.TeAra.govt.nz/en/canterbury-region/page-8
John, W. (2006). 'Canterbury region - Agriculture before 1900. Retrieved from, http://www.TeAra.govt.nz/en/canterbury-region/page-7
John, W. (2006b). Canterbury region - Discovery and settlement. Retrieved from http://www.TeAra.govt.nz/en/canterbury-region/page-6
Johnes, P., & Heathwaite, A. L. (1997). Modelling the impact of land use change on water quality in agricultural catchments. *Hydrological processes, 11*(3), 269-286.
Johnes, P. J. (1999). Understanding lake and catchment history as a tool for integrated lake management. *Hydrobiologia, 395*(0), 41-60. doi:10.1023/A:1017002914903
Juma, D., Wang, H., & Li, F. (2014). Impacts of population growth and economic development on water quality of a lake: case study of Lake Victoria Kenya water. *Environmental Science and Pollution Research, 21*(8), 5737-5746. doi:10.1007/s11356-014-2524-5
Kabata-Pendias, A. (2001). *Trace elements in soils and plants* (3rd ed.. ed.). Boca Raton, Fla.: Boca Raton, Fla. : CRC Press.
Kanemoto-Kataoka, Y., Oyama, K., Oyama, T. M., Ishibashi, H., & Oyama, Y. (2018). Ziram, a dithiocarbamate fungicide, exhibits pseudo-cytoprotective actions against oxidative stress in rat thymocytes: Possible environmental risks. *Environmental Research, 160*, 232-238. doi:10.1016/j.envres.2017.09.027
Karbassi, A., Monavari, S., Bidhendi, G. R. N., Nouri, J., & Nematpour, K. (2008). Metal pollution assessment of sediment and water in the Shur River. *Environmental monitoring and assessment, 147*(1-3), 107.

Kelliher, F. M., Gray, C. W., & Noble, A. D. (2017). Superphosphate fertiliser application and cadmium accumulation in a pastoral soil. *New Zealand Journal of Agricultural Research, 60*(4), 404-422.
Kelly, D., Waters, S. A., Stewart, S., & Moore, D. (2019). *Approaches for the restoration of water quality and aquatic health in Lake Moawhitu*. Retrieved from
Kiekens, L. (1995). *Zinc. In: Alloway, B.J., Ed., Heavy Metals in Soils, 2nd Edition*. London: Blackie Academic and Professional.
Koinig, K. A., Shotyk, W., Lotter, A. F., Ohlendorf, C., & Sturm, M. (2003). 9000 years of geochemical evolution of lithogenic major and trace elements in the sediment of an alpine lake – the role of climate, vegetation, and land-use history. *Journal of Paleolimnology, 30*(3), 307-320. doi:10.1023/A:1026080712312
Koyama, M., Kawashima, M., Takamatsu, T., Glasby, G., & Stoppers, P. (1989). Mineralogy and geochemistry of sediments from Lakes Taupo and Waikaremoana, New Zealand. *New Zealand journal of marine and freshwater research, 23*(1), 121-130.
Kusabs, I. (2017). *Lakes Ngapōuri, Ngahēwa, Tutaeinanga - Monitoring of kōura and common bully using the tau kōura*.
Lambkin, D. C., & Alloway, B. J. (2000). The problem of arsenic interference in the analysis of soils for cadmium by inductively coupled plasma-optical emission spectrometry. *Sci Total Environ, 256*(1), 77-81. doi:10.1016/S0048-9697(00)00475-7
Land Air Water Aotearoa (LAWA). (2017a). Canterbury Lakes Retrieved from https://www.lawa.org.nz/explore-data/canterbury-region/lakes/lake-heron/
Land Air Water Aotearoa (LAWA). (2017b). Canterbury Lakes -Lake Heron Retrieved from https://www.lawa.org.nz/explore-data/canterbury-region/lakes/lake-heron/
Land Monitoring Forum (LMF). (2009). *Land and Soil Monitoring: A guide for SoE and regional council reporting*. Retrieved from New Zealand
Lepp, N. W. (1995). Plants and the chemical elements: Biochemistry, uptake, tolerance and toxicity: Edited by Margaret Farago, VCH Weinheim, Basel (Book Review). In (Vol. 87, pp. 373-373).
Lian, O. B., & Roberts, R. G. (2006). Dating the Quaternary: progress in luminescence dating of sediments. *Quaternary Science Reviews, 25*(19-20), 2449-2468.
Life Systems, I. (1989). *Toxicological profile for cadmium*: Oak Ridge, Tenn.: Oak Ridge National Laboratory.
Lin, C., He, M., Zhou, Y., Guo, W., & Yang, Z. (2008). Distribution and contamination assessment of heavy metals in sediment of the Second Songhua River, China. *Environmental monitoring and assessment, 137*(1-3), 329.
Loganathan, P., Hedley, M. J., Grace, N. D., Lee, J., Cronin, S. J., Bolan, N. S., & Zanders, J. M. (2003). Fertiliser contaminants in New Zealand grazed pasture with special reference to cadmium and fluorine: A review. *Australian Journal of Soil Research, 41*(3), 501-532. doi:10.1071/SR02126
Lotter, A., Amman, B., Beer, J., Sturm, M., & Hajdas, I. (1992). A Step Towards an Absolute Time-Scale for the Late-Glacial: Annually Laminated Sediments from Soppensee (Switzerland). *The Last Deglaciation: Absolute and Radiocarbon Chronologies*.
Lynn, I. (2005). *Lake Wairewa/Lake Forsyth : Potential sources of Phosphorous to the lake* (2005/02). Retrieved from
Ma, L., Wu, J., Abuduwaili, J., & Liu, W. (2016). Geochemical responses to anthropogenic and natural influences in Ebinur Lake sediments of arid Northwest China. *PloS one, 11*(5), e0155819.
Main, M. (2002). Lake Forsyth case study. *Lake Managers' Handbook: Land-Water Interactions. Ministry for the Environment, Wellington, New Zealand*, 61-62.
Marshall, B. (1993). *Recent MAF cadmium residue data.* Paper presented at the Second Cadmium Research Liaison Meeting'.(Ed. J Lee) pp.
Martin, A. P., Turnbull, R. E., Rissmann, C. W., & Rieger, P. (2017). Heavy metal and metalloid concentrations in soils under pasture of southern New Zealand. *Geoderma Regional, 11*, 18-27. doi:10.1016/j.geodrs.2017.08.005
McBride, G., Holland, P., & Wilson, K. (1998). *Investigation of contaminated sheep dipping sites in the Waikato.* Paper presented at the Waste Management Institute New Zealand Conference, Routori, New Zealand

McBride, M. B. (2011). A Comparison of Reliability of Soil Cadmium Determination by Standard Spectrometric Methods. *J Environ Qual, 40*(6), 1863-1869. doi:10.2134/jeq2011.0096
McFadgen, B. G. (2003). *Archaeology of the Wellington Conservancy : Wairarapa : a study in tectonic archaeology*. Wellington, N.Z.: Wellington, N.Z. : Dept. of Conservation.
McGlone, M. S., & Wilmshurst, J. M. (1999). A Holocene record of climate, vegetation change and peat bog development, east Otago, South Island, New Zealand. *Journal of Quaternary Science, 14*(3), 239-254. doi:10.1002/(SICI)1099-1417(199905)14:3<239::AID-JQS438>3.0.CO 2-9
McIntyre, R. (2002). *The canoes of Kupe : a history of Martinborough district*. Wellington, N.Z.: Wellington, N.Z. : Victoria University Press.
McIntyre, R. (2007). Historic heritage of high-country pastoralism: South Island up to 1948. In C. New Zealand. Department of (Ed.). Wellington, N.Z: Wellington, N.Z: Department of Conservation.
McKinnon, M. (2016). 'Marlborough region', Te Ara - the Encyclopedia of New Zealand. Retrieved from http://www.TeAra.govt.nz/en/marlborough-region
McLaren, R. G., Naidu, R., Smith, J., & Tiller, K. G. (1998). Fractionation and distribution of arsenic in soils contaminated by cattle dip. *Journal of Environmental Quality, 27*(2), 348-354. doi:10.2134/jeq1998.00472425002700020015x
McLaughlin, M. J., & Singh, B. R. (1999). Cadmium in soils and plants. In *Cadmium in soils and plants* (pp. 1-9): Springer.
McLeod, D., & Burrows, C. J. (1977). *History of the Cass District*. Christchurch, New Zealand ept of Botany, University of Canterbury.
McWethy, D. B., Whitlock, C., Wilmshurst, J. M., McGlone, M. S., Fromont, M., Li, X., . . . Cook, E. R. (2010). Rapid landscape transformation in South Island, New Zealand, following initial Polynesian settlement. *Proceedings of the National Academy of Sciences, 107*(50), 21343-21348.
Merry, R., Tiller, K. G., & Alston, A. M. (1983). Accumulation of copper, lead and arsenic in some Australian orchard soils. *Australian Journal of Soil Research - AUST J SOIL RES, 21*. doi:10.1071/SR9830549
Miller, J., & Webster-Brown, J. (2013). *Principal Sources of Summer Sediment to Lake Forsyth/Wairewa*. Retrieved from Christchrch, New Zealand http://www.waterways.ac.nz/reportsindex.shtml
Ministry for the Environment. (2019). *Environment Aotearoa 2019*. Wellington, New Zealand: Minstry for the Environment
Ministry for the Environment (MfE). (2006). *New Zealand's Greenhouse Gas Inventory 1990-2004*. Retrieved from wellington, New Zealand
Minstry for the Environment. (2017). *New Zealand's Environmental Reporting Series: Our fresh water 2017*. Wellington, New Zealand: Minstry for the Environment.
Molloy, B. P. J. (1977). *The 'fire history. In "Cass"*. Christchurch, New Zealand Dept of Botany, University of Canterbury.
Moore, L. B. (1970). *Flora of New Zealand / Volume II, Indigenous Tracheophyta (Monocotyledones except Gramineae)*. Wellington, N.Z.: Wellington, N.Z. : Government Printer.
Moss, B., Johnes, P. J., & Phillips, G. L. (1996). The monitoring of ecological quality and the classification of standing waters in temperate regions: a review and proposal based on a worked scheme for British waters. *Biol. Rev, 71*, 301-339.
Mozhdeh, D., Giti Forghani, T., Hadi, G., & Habibollah, G. (2019). Distribution of Potentially Toxic Elements in the Tailings, Mine and Agricultural Soils around the Irankuh Pb-Zn Mine, SW Esfahan. *Journal of Economic Geology, 10*(2), 537-559. doi:10.22067/econg.v10i2.62158
Newsome, P., Wilde, R., & Willoughby, E. (2008). *Land Resource Information System Spatial: Data Layers*: Landcare Research New Zealand.
Newton, K., Amarasiriwardena, D., & Xing, B. (2006). Distribution of soil arsenic species, lead and arsenic bound to humic acid molar mass fractions in a contaminated apple orchard. *Environmental Pollution, 143*(2), 197-205. doi:10.1016/j.envpol.2005.12.001

Nicholson, F. A., Chambers, B. J., Williams, J. R., & Unwin, R. J. (1999). Heavy metal contents of livestock feeds and animal manures in England and Wales. *Bioresource Technology, 70*(1), 23-31. doi:10.1016/S0960-8524(99)00017-6

Nolting, R., Ramkema, A., & Everaarts, J. (1999). The geochemistry of Cu, Cd, Zn, Ni and Pb in sediment cores from the continental slope of the Banc d'Arguin (Mauritania). *Continental Shelf Research, 19*(5), 665-691.

Norton, S. A., & Kahl, J. S. (1991). Progress in understanding the chemical stratigraphy of metals in lake sediments in relation to acidic precipitation. *Hydrobiologia* doi:https://doi.org/10.1007/BF00050935

Organisation for Economic Co-operation and Development. (2001). *OECD – Sustainable Development: Critical Issues* (Vol. 12): Emerald Group Publishing Limited.

Pace, M. L., Knauer, G. A., Karl, D. M., & Martin, J. H. (1987). Primary production, new production and vertical flux in the eastern Pacific Ocean. *Nature, 325*(6107), 803-804.

Pearson, L. K. (2012). *Sediment-Pore Water Chemistry of Taupo Volcanic Zone Lakes and the Effect Trophic State has on Exchange with the Water Column.* University of Waikato,

Pearson, L. K., Hendy, C. H., Hamilton, D. P., & Silvester, W. B. (2012). Nitrogen-15 isotope enrichment in benthic boundary layer gases of a stratified eutrophic iron and manganese rich lake. *Aquatic geochemistry, 18*(1), 1-19.

Pereira, E., Baptista-Neto, J. A., Smith, B. J., & Mcallister, J. J. (2007). The contribution of heavy metal pollution derived from highway runoff to Guanabara Bay sediments: Rio de Janeiro/Brazil. *Anais da Academia Brasileira de Ciências, 79*(4), 739-750.

Petrie, L. M. (1963). *From Bush to Cocksfoot: An Essay on the Destruction of Banks Peninsulas¢ Forests.* Canterbury University Canterbury, New Zealand

Pettinga, J., Yetton, M. D., Van Dissen, R. J., & Downes, G. (2001). Earthquake Source Identification and Characterisation for the Canterbury Region, South Island, New Zealand. *Bulletin of the New Zealand Society for Earthquake Engineering, 34*, 282-317.

Pickrill, R., & Irwin, J. (1983). Sedimentation in a deep glacier-fed lake—Lake Tekapo, New Zealand. *Sedimentology, 30*(1), 63-75.

Plum, L., Rink, L., & Haase, H. (2010). The Essential Toxin: Impact of Zinc on Human Health. *International journal of environmental research and public health, 7*, 1342-1365. doi:10.3390/ijerph7041342

Prasad, A. S. (2001). Discovery of human zinc deficiency: impact on human health. *Nutrition, 17*(7-8), 685-687. doi:10.1016/S0899-9007(01)00598-6

Praveena, S., Radojevic, M., Abdullah, M., & Aris, A. Z. (2008). Application of sediment quality guidelines in the assessment of mangrove surface sediment in Mengkabong Lagoon, Sabah, Malaysia. *Iranian Journal of Environmental Health Science & Engineering, 5*.

Pugh, J., & Shulmeister, J. (2010). Holocene vegetation history of a high-elevation (1200 m) site in the Lake Heron Basin, inland Canterbury, New Zealand. *Altered ecologies: fire, climate and human influence on terrestrial landscapes. Terra Australis, 32*, 69-81.

Qi, S., Leipe, T., Rueckert, P., Di, Z., & Harff, J. (2010). Geochemical sources, deposition and enrichment of heavy metals in short sediment cores from the Pearl River Estuary, Southern China. *Journal of marine systems, 82*, S28-S42. doi:10.1016/j.jmarsys.2010.02.003

Quinton, J., & Catt, J. (2007). Enrichment of Heavy Metals in Sediment Resulting from Soil Erosion on Agricultural Fields. *Environmental science & technology, 41*, 3495-3500. doi:10.1021/es062147h

Rainbow, P. (2018). *Trace Metals in the Environment and Living Organisms: The British Isles as a Case Study*. Cambridge, UK: Cambridge University Press,.

Ramlal, P., Hecky, R., Bootsma, H., Schiff, S., & Kingdon, M. (2003). Sources and Fluxes of Organic Carbon in Lake Malawi/Nyasa. *Journal of Great Lakes Research - J GREAT LAKES RES, 29*, 107-120. doi:10.1016/S0380-1330(03)70542-5

Reay, P. (1972). The accumulation of arsenic from arsenic-rich natural waters by aquatic plants. *Journal of applied ecology*, 557-565.

Reddy, P. V. L., Hernandez-Viezcas, J. A., Peralta-Videa, J. R., & Gardea-Torresdey, J. L. (2016). Lessons learned: Are engineered nanomaterials toxic to terrestrial plants? *Science of the Total Environment, 568*, 470-479. doi:10.1016/j.scitotenv.2016.06.042

Rehman, M., Liu, L., Wang, Q., Saleem, M., Bashir, S., Ullah, S., & Peng, D. (2019). Copper environmental toxicology, recent advances, and future outlook: a review. *Environmental Science and Pollution Research, 26*(18), 18003-18016. doi:10.1007/s11356-019-05073-6

Reid, M., Wybrow, R., & Woodward, C. (2004). Managing Te Roto o Wairewa : lessons from the past. *Water & atmosphere, 12*(4), 12-13.

Ricciardi, A., & Rasmussen, J., B. (1999). Extinction Rates of North American Freshwater Fauna. *Conservation Biology, 13*(5), 1220-1222. doi:10.1046/j.1523-1739.1999.98380.x

Robinson, B., Clothier, B., Bolan, N., Mahimairaja, S., Greven, M., Moni, C., . . . Milne, G. (2004). *Arsenic in the New Zealand environment.* Paper presented at the 3rd Australian New Zealand Soils Conference.

Robinson, B., Kim, N., Marchetti, M., Moni, C., Schroeter, L., van den Dijssel, C., . . . Clothier, B. (2006). Arsenic hyperaccumulation by aquatic macrophytes in the Taupo Volcanic Zone, New Zealand. *Environmental and Experimental Botany, 58*(1-3), 206-215.

Rodda, J. C., & Shiklomanov, I. A. (2003). *World water resources at the beginning of the Twenty-First Century*. Cambridge United Kingdom: Cambridge University Press.

Saarinen, T. J. (2010). Varves of Lehmilampi (Eastern Finland). Retrieved from http://users.utu.fi/tijusa/

Salati, S., & Moore, F. (2010). Assessment of heavy metal concentration in the Khoshk River water and sediment, Shiraz, Southwest Iran. *Environmental monitoring and assessment, 164*(1-4), 677-689.

Salomons, W., De Rooij, N., Kerdijk, H., & Bril, J. (1987). Sediments as a source for contaminants? *Hydrobiologia, 149*(1), 13-30.

Schallenberg, M., & Schallenberg, L. A. (2013). *Lake Forsyth/Wairewa: a literature review*: Environment Canterbury Regional Council.

Schmidt, R., Koinig, K. A., Thompson, R., & Kamenik, C. (2002). A multi proxy core study of the last 7000 years of climate and alpine land-use impacts on an Austrian mountain lake (Unterer Landschitzsee, Niedere Tauern). *Palaeogeography, Palaeoclimatology, Palaeoecology, 187*(1-2), 101-120. doi:10.1016/S0031-0182(02)00511-4

Selvaraj, K., Mohan, V. R., & Szefer, P. (2004). Evaluation of metal contamination in coastal sediments of the Bay of Bengal, India: geochemical and statistical approaches. *Marine pollution bulletin, 49*(3), 174-185.

Shaghla, P., Jasmeen, B., & Bushra, P. (2018). A Literature Review On Land Use Land Cover Changes. In: Zenodo.

Smedley, P. L., & Kinniburgh, D. G. (2002). A review of the source, behaviour and distribution of arsenic in natural waters. *Applied geochemistry, 17*(5), 517-568.

Smith, C. M. (1993). *Towards sustainable agriculture : freshwater quality in New Zealand and the influence of agriculture*. Wellington, N.Z.: Wellington, N.Z. : MAF Policy.

Smith, D. G., & Williamson, R. B. (1986). Heavy metals in the New Zealand aquatic environment.

Smol, J. P. (2002). *Tracking Environmental Change Using Lake Sediments. Vol. 3*: Dordrecht : Springer Netherlands.

Smol, J. P., & Cumming, B. F. (2000). TRACKING LONG-TERM CHANGES IN CLIMATE USING ALGAL INDICATORS IN LAKE SEDIMENTS. *Journal of Phycology, 36*(6), 986-1011. doi:10.1046/j.1529-8817.2000.00049.x

Soons, J. M. (1998). Recent Coastal Change in Canterbury- the case of Lake Forsyth/Wairewa. *New Zealand Geographer, 54*(1), 7-14. doi:10.1111/j.1745-7939.1998.tb00516.x

Soons, J. M., Shulmeister, J., & Holt, S. (1997). The Holocene evolution of a well nourished gravelly barrier and lagoon complex, Kaitorete “Spit”, Canterbury, New Zealand. *Marine Geology, 138*(1-2), 69-90. doi:10.1016/S0025-3227(97)00003-0

Stefanidou, M., Maravelias, C., Dona, A., & Spiliopoulou, C. (2006). Zinc: A multipurpose trace element. *Archives of toxicology, 80*, 1-9. doi:10.1007/s00204-005-0009-5

Stilwell, D., & Graetz, T. (2001). Copper, Chromium, and Arsenic Levels in Soil Near Highway Traffic Sound Barriers Built Using CCA Pressure-Treated Wood. *Bulletin of Environmental Contamination and Toxicology, 67*, 0303-0308. doi:10.1007/s00128-001-0125-8

Stoffers, P., Glasby, G., Plueger, W., & Walter, P. (1983). Reconnaissance survey of the mineralogy and geochemistry of some New Zealand lake and nearshore sediments. *New Zealand journal of marine and freshwater research, 17*(4), 461-480.

Swarbrick, N. (2015). Waikato region', Te Ara - the Encyclopedia of New Zealand. Retrieved from http://www.TeAra.govt.nz/en/waikato-region

Swetnam, T., Allen, C., & Betancourt, J. (1999). Applied Historical Ecology: Using the Past to Manage for the Future. *Ecological Applications, 9*, 1189-1206. doi:10.1890/1051-0761(1999)009[1189:AHEUTP]2.0.CO;2

Tanner, C. C., & Clayton, J. S. (1990). Persistence of arsenic 24 years after sodium arsenite herbicide application to Lake Rotoroa, Hamilton, New Zealand. *New Zealand journal of marine and freshwater research, 24*(2), 173-179. doi:10.1080/00288330.1990.9516412

Tanner, P. A., Leong, L. S., & Pan, S. M. (2000). Contamination of heavy metals in marine sediment cores from Victoria Harbour, Hong Kong. *Marine pollution bulletin, 40*(9), 769-779.

Taylor, M. D. (2011). *Soil quality and trace element monitoring in the Waikato Region 2009*. Retrieved from Hamilton, N.Z:

Taylor, R., & Smith, I. (1997). *The state of New Zealand's environment 1997*. Wellington, N.Z.: Wellington, N.Z. : Ministry for the Environment.

Teng, Y., Yang, J., Zuo, R., & Wang, J. (2011). Impact of urbanization and industrialization upon surface water quality: A pilot study of Panzhihua mining town. *Journal of Earth Science, 22*(5), 658-668. doi:10.1007/s12583-011-0217-2

Thomson, J., Nixon, S., Croudace, I., Pedersen, T., Brown, L., Cook, G., & MacKenzie, A. (2001). Redox-sensitive element uptake in north-east Atlantic Ocean sediments (Benthic Boundary Layer Experiment sites). *Earth and Planetary Science Letters, 184*(2), 535-547.

Tilman, D. (1999). Global environmental impacts of agricultural expansion: the need for sustainable and efficient practices. *Global environmental impacts of agricultural expansion: the need for sustainable and efficient practices, 96*(11), 5995-6000.

UNESCO World Water Assessment Programme (UN WWAP). (2019). *The United Nations World Water Development Report 2019: Leaving No One Behind*. Paris, France: UNESCO.

United Nations Environment Programme (UNEP). (1996). *Groundwater: a threatened resource*. Nairobi, Kenya: UNEP.

United Nations World Water Assessment Programme (UN WWAP). (2003). *The World Water Development Report 1: Water for People, Water for Life*. Paris, France: UNESCO.

Verburg, P., Hamill, K., Unwin, M., & Abell, J. (2010). *Lake water quality in New Zealand 2010: Status and trends*. Retrieved from Hamilton, New Zealand:

Vitousek, P., Mooney, H., Lubchenco, J., & Melillo, J. (1997). Human Domination of Earth's Ecosystems. *Science, 277*. doi:10.1007/978-0-387-73412-5_1

von Gunten, H. R., & Moser, R. N. J. (1993). How reliable is the ^{210}Pb dating method? Old and new results from Switzerland. *Paleolimnol*. doi:https://doi.org/10.1007/BF00677518

Ward, N. I. (1990). Multielement contamination of British motorway environments. *Science of the Total Environment, 93*(C), 393-401. doi:10.1016/0048-9697(90)90130-M

Waterlot, C., & Douay, F. (2009). The problem of arsenic interference in the analysis of Cd to evaluate its extractability in soils contaminated by arsenic. *Talanta, 80*(2), 716-722. doi:10.1016/j.talanta.2009.07.053

Waters, A. S. (2016). Phosphorus dynamics in a shallow coastal lake system, Canterbury, New Zealand.

Waters, S. A. (2016). *Phosphorous Dynamics in shallow coastal lak system, Canterbury, New Zealand* (PhD). University of Canterbury Canterbury, New Zealand

Weng, H.-X., Zhang, X.-M., Chen, X.-H., & Wu, N.-Y. (2003). The stability of the relative content ratios of Cu, Pb and Zn in soils and sediments. *Environmental Geology, 45*(1), 79-85.

Westphal, H., Halfar, J., & Freiwald, A. (2010). Heterozoan carbonates in subtropical to tropical settings in the present and past. *International Journal of Earth Sciences, 99*(1), 153-169. doi:10.1007/s00531-010-0563-9

Whitton, B., Say, P., & Jupp, B. (1982). Accumulation of zinc, cadmium and lead by the aquatic liverwort Scapania. *Environmental Pollution Series B, Chemical and Physical, 3*(4), 299-316.

Wilmshurst, J. M., Higham, T. F., Allen, H., Johns, D., & Phillips, C. (2004). Early Maori settlement impacts in northern coastal Taranaki, New Zealand. *New Zealand Journal of Ecology*, 167-179.

Wolfe, A. P., & Härtling, J. W. (1997). Early Holocene Trace Metal Enrichment in Organic Lake Sediments, Baffin Island, Arctic Canada. *Arctic and Alpine Research, 29*(1), 24-31. doi:10.2307/1551833

Woodward, C. A., & Shulmeister, J. (2005). A Holocene Record of Human Induced and Natural Environmental Change from Lake Forsyth (Te Wairewa), New Zealand. *Journal of Paleolimnology, 34*(4), 481-501. doi:10.1007/s10933-005-5708-7

Xiong, X., Yanxia, L., Wei, L., Lin, C., Wei, H., & Ming, Y. (2010). Copper content in animal manures and potential risk of soil copper pollution with animal manure use in agriculture. *Resources, Conservation and Recycling, 54*, 985-990. doi:10.1016/j.resconrec.2010.02.005

Zagury, G., Samson, R., & Deschênes, L. (2003). Occurrence of Metals in Soil and Ground Water Near Chromated Copper Arsenate–Treated Utility Poles. *Journal of Environmental Quality, 32*, 507-514. doi:10.2134/jeq2003.0507

Zahra, A., Hashmi, M. Z., Malik, R. N., & Ahmed, Z. (2014). Enrichment and geo-accumulation of heavy metals and risk assessment of sediments of the Kurang Nallah—feeding tributary of the Rawal Lake Reservoir, Pakistan. *Science of the Total Environment, 470*, 925-933.

Zheng, L., Wu, K., Li, Y., Qi, Z., Han, D., Zhang, B., . . . Huo, X. (2008). Blood lead and cadmium levels and relevant factors among children from an e-waste recycling town in China. *Environmental Research, 108*(1), 15-20. doi:10.1016/j.envres.2008.04.002

Appendix A

Determining concentration of trace elements

This section shows appendices of the methods described in section 3.3 of the Chapter 3 for determination of concentration of trace elements in dry sediments .

A.1 Digestion process raw data (weight and dilution factors)

This section presents weight of dry sediments, weight of C-tube, weight of C-tube + extract, weight of extract and dilution factors as derived during digestion process described in section 3.3.3.

Table A.1 Table A1 showing weight of dry sediments, weight of C-tube, weight of C-tube + extract, weight of extract and dilution factors for Lake Ngāpouri

LAKE NGĀPOURI					
Depth (cm)	**Weight (g) of dry sediments**	**Weight of C-tube**	**Weight of C-tube + extract**	**Weight of extract**	**Dilution factor**
1	0.1025	6.6491	17.7353	11.0862	108.1580
3	0.1066	6.6562	17.9429	11.2867	105.8789
6	0.108	6.6768	17.4104	10.7336	99.3852
9	0.1052	6.68	17.6114	10.9314	103.9106
12	0.1053	6.709	17.9254	11.2164	106.5185
15	0.1114	6.6641	17.3653	10.7012	96.0610
18	0.1006	6.6855	17.6532	10.9677	109.0228
21	0.1111	6.7065	17.1576	10.4511	94.0693
24	0.1026	6.6546	18.0874	11.4328	111.4308
27	0.108	6.656	17.5844	10.9284	101.1889
30	0.1026	6.6504	17.5061	10.8557	105.8060
33	0.1101	6.6568	17.7708	11.114	100.9446
39	0.1089	6.6773	17.1914	10.5141	96.5482
45	0.104	6.7087	17.1472	10.4385	100.3701
51	0.1131	6.6816	17.3711	16.6895	94.5137
57	0.1133	6.677	18.5835	11.9065	105.0882
63	0.1115	6.6588	17.7134	11.0546	99.1443
69	0.1128	6.6593	17.1304	10.4711	92.8289
75	0.1113	6.6777	17.5932	10.9155	98.0727
81	0.1046	6.6784	17.206	10.5276	100.6462
BLK1	0	6.73	17.148	10.418	-
BLK2	0	6.6738	17.6169	10.9431	-

Table A.2 Weight of dry sediments, weight of C-tube, weight of C-tube + extract, weight of extract and dilution factors for Lake Tutaeinanga.

LAKE TUTAEINANGA					
Depth (cm)	**Weight (g) of dry sediments**	**Weight of C-tube**	**Weight of C-tube + extract**	**Weight of extract**	**Dilution factor**
1	0.0655	6.6836	14.5718	7.8882	120.4305
2	0.1160	6.7009	19.5847	12.8838	111.0672
3	0.1240	6.9920	18.5848	11.5928	93.4903
4	0.0992	6.6647	16.7768	10.1121	101.9365
5	0.1070	6.6623	17.0788	10.4165	97.3505
6	0.1073	6.6597	18.0412	11.3815	106.0718
7	0.1080	6.6862	18.1072	11.421	105.7500
8	0.0942	6.6751	18.1172	11.4421	121.4660
9	0.0984	6.6709	16.9159	10.245	104.1159
10	0.0990	6.6744	17.5304	10.856	109.6566
11	0.1008	6.7117	17.1874	10.4757	103.9256
12	0.1000	6.6813	18.4486	11.7673	117.6730
13	0.1011	6.6654	17.1787	10.5133	103.9891
14	0.1043	6.6804	16.8001	10.1197	97.0249
15	0.1135	6.7034	17.8054	11.102	97.8150
16	0.1073	6.7518	16.8315	10.0797	93.9394
17	0.1148	6.699	16.5494	9.8504	85.8049
18	0.1042	6.6797	18.981	12.3013	118.0547
19	0.1117	6.6637	19.2003	12.5366	112.2346
20	0.0987	6.6881	17.5043	10.8162	109.5866
21	0.1057	6.6871	19.3144	12.6273	119.4636
22	0.1093	6.7272	18.7295	12.0023	109.8106
23	0.1009	6.6854	19.0043	12.3189	122.0902
24	0.1028	6.6792	17.6239	10.9447	106.4660
25	0.1042	6.6773	17.4404	10.7631	103.2927
26	0.1031	6.6851	17.8459	11.1608	108.2522
27	0.1005	6.6862	18.1722	11.486	114.2886
28	0.1052	6.6888	17.8048	11.116	105.6654
29	0.1051	6.6581	17.88	11.2219	106.7735
30	0.112	6.6696	18.7129	12.0433	107.5295
33	0.1123	6.6776	19.1733	12.4957	111.2707
36	0.121	6.6608	19.78	13.1192	108.4231
39	0.1085	6.651	18.9074	12.2564	112.9622
42	0.0979	6.6688	18.1391	11.4703	117.1634
45	0.1023	6.6811	18.0086	11.3275	110.7283
48	0.0982	6.6994	17.5718	10.8724	110.7169
51	0.1064	6.6691	18.3035	11.6344	109.3459
54	0.1100	6.6802	18.9578	12.2776	111.6145
57	0.1227	6.693	20.9759	14.2829	116.4051
BLk1	0	6.6903	18.0253	11.335	-
BLK2	0	6.6502	17.7991	11.1489	-

Table A.3 Weight of dry sediments, weight of C-tube, weight of C-tube + extract, weight of extract and dilution factors for Lake Forsyth.

LAKE FORSYTH					
Depth (cm)	**Weight (g) of dry sediments**	**Weight of C-tube**	**Weight of C-tube + extract**	**Weight of extract**	**Dilution factor**
1	0.1104	6.7215	18.5401	11.8186	107.0525
3	0.1074	6.6566	17.3053	10.6487	99.1499
6	0.1165	6.6526	17.3064	10.6538	91.4489
9	0.1175	6.6792	17.7374	11.0582	94.1123
12	0.1064	6.6794	17.6984	11.019	103.5620
15	0.1088	6.6596	17.2497	10.5901	97.3355
18	0.113	6.6439	17.232	10.5881	93.7000
21	0.1063	6.679	17.993	11.314	106.4346
24	0.0973	6.7149	17.8179	11.103	114.1110
27	0.1185	6.6516	18.2585	11.6069	97.9485
30	0.1042	6.6792	17.7546	11.0754	106.2898
33	0.1115	6.6625	17.7705	11.108	99.6233
36	0.1076	6.6585	17.3088	10.6503	98.9805
39	0.106	6.674	17.8302	11.1562	105.2472
42	0.1013	6.6745	16.9533	10.2788	101.4689
45	0.1109	6.6696	17.8962	11.2266	101.2317
48	0.1047	6.6843	17.2582	10.5739	100.9924
51	0.109	6.6783	17.1162	10.4379	95.7606
54	0.1088	6.7685	17.2654	10.4969	96.4789
60	0.1022	6.6843	16.9974	10.3131	100.9110
66	0.102	6.7067	17.8194	11.1127	108.9480
72	0.114	6.6832	17.8182	11.135	97.6754
78	0.101	6.6725	16.616	9.9435	98.4505
84	0.112	6.6875	17.5258	10.8383	96.7705
BLK1	0	6.6787	18.1968	11.5181	-
BLK2	0	6.6668	18.11	11.4432	-
BLK3	0	6.7059	17.4721	10.7662	-

Table A.4 Weight of dry sediments, weight of C-tube, weight of C-tube + extract, weight of extract and dilution factors for Lake Pearson.

LAKE PEARSON					
Depth (cm)	**Weight (g) of dry sediments**	**Weight of C-tube**	**Weight of C-tube + extract**	**Weight of extract**	**Dilution factor**
1	0.102	6.714	17.2343	10.5203	103.1401961
3	0.1067	6.7098	17.3306	10.6208	99.5388941
6	0.1014	6.647	17.3052	10.6582	105.1104536
9	0.1092	6.6839	18.141	11.4571	104.9184982
12	0.1067	6.6525	17.3213	10.6688	99.98875351
15	0.1039	6.6793	17.5638	10.8845	104.759384
18	0.1049	6.6643	17.9711	11.3068	107.7864633
21	0.0992	6.642	17.3033	10.6613	107.4727823
24	0.1013	6.6566	17.4009	10.7443	106.0641658
27	0.0996	6.6805	18.0377	11.3572	114.0281124
30	0.1066	6.6799	17.2324	10.5525	98.99155722
33	0.1001	6.6836	17.5488	10.8652	108.5434565
36	0.1064	6.6492	17.3921	10.7429	100.9671053
39	0.1004	6.7085	18.3927	11.6842	116.376494
42	0.1017	6.6482	17.295	10.6468	104.6882989
48	0.1035	6.646	17.2703	10.6243	102.6502415
54	0.1084	6.7124	18.5643	11.8519	109.3348708
60	0.1049	6.6404	17.0579	10.4175	99.30886559
66	0.1062	6.6733	17.4913	10.818	101.8644068
72	0.1066	6.6865	17.1267	10.4402	97.9380863
78	0.1017	6.676	17.296	10.62	104.4247788
84	0.1048	6.7322	16.9677	10.2355	97.66698473
BLK	0	6.6742	17.1485	10.4743	-

Table A.5 Weight of dry sediments, weight of C-tube, weight of C-tube + extract, weight of extract and dilution factors for Lake Heron.

LAKE HERON					
Depth (cm)	**Weight (g) of dry sediments**	**Weight of C-tube**	**Weight of C-tube + extract**	**Weight of extract**	**Dilution factor**
1	0.1005	6.6808	17.3339	10.6531	106.000995
3	0.1044	6.6759	17.7937	11.1178	106.4923372
6	0.1055	6.6791	17.5987	10.9196	103.5033175
9	0.1014	6.6839	17.0577	10.3738	102.3057199
12	0.1018	6.6856	17.6101	10.9245	107.3133595
15	0.1011	6.7298	17.2038	10.474	103.6003956
18	0.1021	6.6684	17.2395	10.5711	103.5367287
21	0.1061	6.6684	17.676	11.0076	103.7474081
24	0.1021	6.6792	17.5236	10.8444	106.2135162
27	0.1012	6.6726	17.3036	10.631	105.0494071
30	0.1076	6.6727	17.4824	10.8097	100.4618959
36	0.1035	6.6854	18.0144	11.329	109.4589372
42	0.1015	6.6819	17.5171	10.8352	106.7507389
48	0.108	6.6796	17.0669	10.3873	96.1787037
54	0.116	6.6758	17.4456	10.7698	92.84310345
60	0.0999	6.6491	17.4445	10.7954	108.0620621
66	0.1013	6.6614	17.4212	10.7598	106.2171767
72	0.1087	6.667	17.1908	10.5238	96.8150874
78	0.1084	6.7085	17.5505	10.842	100.0184502
84	0.1179	6.6888	17.6295	10.9407	92.79643766
BK1	0	6.6801	17.6394	10.9593	-

Table A.6 Weight of dry sediments, weight of C-tube, weight of C-tube + extract, weight of extract and dilution factors for Lake Moawhitu.

LAKE MOAWHITU					
Depth (cm)	**Weight (g) of dry sediments**	**Weight of C-tube**	**Weight of C-tube + extract**	**Weight of extract**	**Dilution factor**
1	0.1042	6.6463	17.5347	10.8884	104.4952015
3	0.0991	6.6561	16.9582	10.3021	103.9566095
6	0.1130	6.6767	16.9402	10.2635	90.82743363
9	0.1090	6.6484	17.5143	10.8659	99.68715596
12	0.1075	6.6500	17.9252	11.2752	104.8855814
15	0.1048	6.6626	17.9541	11.2915	107.7433206
18	0.1018	6.7347	17.5348	10.8001	106.0913556
21	0.1038	6.6755	17.6244	10.9489	105.4807322
24	0.0994	6.6594	17.1993	10.5399	106.0352113
27	0.1027	6.6755	17.1830	10.5075	102.3125609
30	0.1016	6.6775	17.7865	11.109	109.3405512
33	0.0980	6.6868	17.9653	11.2785	115.0867347
39	0.1004	6.7167	17.0752	10.3585	103.1723108
45	0.1064	6.6686	17.2343	10.5657	99.30169173
51	0.1108	6.6365	17.8662	11.2297	101.351083
57	0.1021	6.6856	17.1962	10.5106	102.9441724
63	0.0994	6.6784	17.2870	10.6086	106.7263581
69	0.1058	6.6752	17.4633	10.7881	101.9669187
75	0.1032	6.6561	17.2961	10.6400	103.1007752
81	0.1024	6.6802	17.2527	10.5725	103.2470703
BLK 1	0	6.6576	17.8940	11.2364	-
BLK 2	0	6.6793	18.1874	11.5081	-

Table A. 7 Weight of dry sediments, weight of C-tube, weight of C-tube + extract, weight of extract and dilution factors for F10 and F10 cores collected from Lake Forsyth by previous student as described in section 3.3.6 of chapter 3.

LAKE FORSYTH PREVIOUS CORES					
Depth (cm)	**Weight (g) of dry sediments**	**Weight of C-tube**	**Weight of C-tube + extract**	**Weight of extract**	**Dilution factor**
F10 core					
1	0.1227	6.6939	19.2742	12.5803	102.5289
2	0.1164	6.6878	18.5924	11.9046	102.2732
3	0.1038	6.7399	17.5083	10.7684	103.7418
4	0.1114	6.6814	18.3416	11.6602	104.6697
5	0.1110	6.7296	17.7868	11.0572	99.6144
7	0.1056	6.6882	18.7242	12.0360	113.9773
9	0.1075	6.6756	18.5570	11.8814	110.5247
11	0.1096	6.6763	17.9130	11.2367	102.5246
13	0.1255	6.6691	18.4871	11.8180	94.1673
15	0.1208	6.6573	17.7764	11.1191	92.0455
20	0.1080	6.7138	17.7853	11.0715	102.5139
25	0.1165	6.6804	18.4899	11.8095	101.3691
Blank	0.0000	6.6500	18.8576	12.2076	
F11 core					
1	0.5074	13.2620	63.9685	50.7065	99.9340
2	0.5028	13.0997	62.7754	49.6757	98.7981
3	0.5165	13.1795	65.2828	52.1033	100.8776
4	0.5037	13.1997	63.5902	50.3905	100.0407
5	0.5016	13.0860	64.2705	51.1845	102.0425
7	0.5124	13.2272	63.5822	50.3550	98.2728
9	0.5032	13.3310	67.8895	54.5585	108.4231
11	0.5135	13.2866	63.5977	50.3111	97.9768
13	0.5030	13.2646	63.9140	50.6494	100.6946
15	0.4995	13.0518	63.8268	50.7750	101.6517
20	0.5028	13.1956	63.8842	50.6886	100.8126
25	0.5065	13.1656	63.7352	50.5696	99.8413
Blank	0.0000	13.2710	62.2489	48.9779	#DIV/0!

A.2 Concentration of Trace elements in solution – ICP-OES ($C_{extract}$)

This section presents results of concentration of extract of trace elements from ICP-OES analysis as described in section 3.3.4 in chapter 3.

Table A.8 Concentration of extract of trace elements after ICP-OES analysis – Cextract (Lake Tutaeinanga)

LAKE TUTAEINANGA – $C_{extract}$												
Depth cm	**Cd (ppm)**	**As (ppm)**	**Cu(ppm)**	**Zn (ppm)**	**P (ppm)**	**Pb (ppm)**	**Fe(ppm)**	**Mn (ppm)**	**Al (ppm)**	**Cr (ppm)**	**Ni (ppm)**	**V (ppm)**
1	0.0145	0.2656	0.2963	1.9571	30.3600	0.1653	168.6755	2.2683	146.2380	0.0622	0.0569	1.2800
2	0.0114	0.2999	0.3815	1.6656	20.7800	0.1526	204.3552	1.7312	121.7460	0.0417	0.0535	1.3400
3	0.0175	0.2839	0.4449	1.8844	23.6000	0.1614	204.8360	1.9298	169.1110	0.0492	0.0530	1.4900
4	0.0098	0.2125	0.5848	1.4284	15.8200	0.1618	128.1982	1.7754	153.0230	0.0429	0.1301	1.5400
5	0.0115	0.2446	0.3799	1.6093	19.4500	0.1892	134.4626	2.2798	184.0380	0.0501	0.0412	1.7900
6	0.0088	0.2100	0.2127	1.3002	16.0400	0.1412	106.2008	2.1046	176.0960	0.0455	0.0301	1.4300
7	0.0100	0.2078	0.2494	1.2543	18.2100	0.1625	103.3141	2.4604	195.8910	0.0506	0.0283	1.5300
8	0.0102	0.2298	0.2029	1.3370	20.0600	0.1704	112.1050	2.6652	205.5680	0.0547	0.0345	1.6200
9	0.0090	0.2116	0.1610	1.2407	14.9000	0.1388	113.1165	2.0347	164.0600	0.0408	0.0317	1.4800
10	0.0073	0.1616	0.1548	0.9819	11.6300	0.1470	89.1811	2.0362	162.5820	0.0453	0.0307	1.5800
11	0.0064	0.1992	0.1364	0.8174	10.3900	0.1304	99.0966	1.8591	150.9060	0.0338	0.0249	1.4200
12	0.0067	0.1484	0.1065	1.0589	12.1900	0.1134	78.0410	2.4700	184.2040	0.0426	0.0203	1.4500
13	0.0043	0.1391	0.0928	0.6561	7.0900	0.0859	74.5633	1.4336	116.5380	0.0251	0.0155	1.0500
14	0.0060	0.1554	0.0927	0.7271	10.4300	0.1017	84.1746	2.0724	172.3860	0.0355	0.0156	1.4800
15	0.0062	0.1341	0.0948	0.6957	11.8500	0.1055	83.1537	2.2876	179.7030	0.0398	0.0175	1.4100
16	0.0070	0.1611	0.1181	0.9022	13.0700	0.1199	95.7979	2.4674	206.1040	0.0408	0.0222	1.6400
17	0.0067	0.1687	0.1106	0.8223	13.1500	0.1197	102.6359	2.5839	207.8460	0.0912	0.0177	1.7200
18	0.0059	0.2463	0.1683	0.9407	9.6300	0.1252	99.7664	1.8537	149.5440	0.0374	0.0255	1.4000
19	0.0048	0.1432	0.0872	0.7399	9.9500	0.1009	75.4679	2.2078	152.9630	0.0337	0.0157	1.4400
20	0.0033	0.1536	0.0765	0.5426	8.1400	0.0917	74.7882	1.9643	136.9330	0.0322	0.0140	1.4500
21	0.0038	0.1516	0.0714	0.6033	6.8700	0.0863	65.7776	1.9129	121.1750	0.0328	0.0116	1.3000
22	0.0040	0.1634	0.0996	1.2732	7.7600	0.0987	77.1097	2.0617	148.6670	0.0345	0.0120	1.5000
23	0.0029	0.1399	0.0666	1.0277	6.6400	0.0812	58.0570	1.7639	119.7060	0.0285	0.0099	1.2400
24	0.0034	0.1380	0.0508	0.7256	4.4100	0.0657	70.3516	1.6330	107.3550	0.0287	0.0082	1.9600

25	0.0028	0.3014	0.0743	1.0572	6.5200	0.0967	110.5321	2.4521	124.7880	0.0413	0.0129	2.6900
26	0.0019	0.1199	0.0494	0.5286	4.5500	0.0680	65.8028	1.7069	88.4960	0.0294	0.0083	1.5800
27	0.0013	0.0865	0.0439	0.6387	3.9600	0.0625	54.8239	1.5976	87.0750	0.0289	0.0052	1.1600
28	0.0014	0.0617	0.0470	0.3452	4.0300	0.0669	56.6096	1.6551	93.3480	0.0305	0.0031	1.1300
29	0.0020	0.0664	0.0452	0.5075	3.7700	0.0686	65.5438	1.6154	108.4730	0.0294	0.0046	1.2900
30	0.0018	0.0621	0.0429	0.4655	3.5800	0.0669	59.9749	1.5985	104.4130	0.0291	0.0046	1.2500
33	0.0015	0.0965	0.0453	0.4981	3.4800	0.0675	69.4488	1.7068	125.5200	0.0344	0.0069	1.5900
36	0.0017	0.1212	0.0543	0.3992	3.6100	0.0773	74.0624	1.8259	147.4780	0.0379	0.0071	1.9300
39	0.0017	0.0975	0.0513	0.7451	2.9500	0.0730	68.8575	1.4828	117.6400	0.0364	0.0118	2.0900
42	0.0049	0.1942	0.0421	0.6338	2.9400	0.0596	79.0439	1.4152	106.8950	0.0318	0.0110	2.1500
45	0.0027	0.2723	0.0470	0.6816	3.0400	0.0599	110.1137	1.3459	104.0090	0.0302	0.0107	2.1300
48	0.0023	0.2114	0.0581	0.7984	2.3000	0.0818	83.6784	1.1944	128.5750	0.0313	0.0087	1.6100
51	0.0045	0.4715	0.0699	1.2735	3.2900	0.0836	152.0186	1.2425	116.2900	0.0451	0.0180	1.9400
54	0.0036	0.2561	0.0977	1.6424	4.4400	0.1106	110.2725	1.5725	163.4350	0.0393	0.0126	2.8300
57	0.0033	0.1306	0.0809	0.6598	3.5500	0.1174	60.8653	1.6093	185.4680	0.0414	0.0133	2.1600
BLk1	0.0004	-0.0013 u	0.0038	0.1015	0.0400	0.0009 u	0.0792	0.0016	0.1840	0.0010	-0.0015 u	-0.03 u
BLK2	0.0000 u	-0.0021 u	0.0029	0.0807	0.0200	-0.0012 u	0.0412	0.0012	0.0640	-0.0005 u	-0.0032 u	-0.03 u
26R	0.0082	0.2519	0.1780	2.4088	13.4000	0.1644	127.2858	2.7002	221.0260	0.0475	0.0297	1.8400

Table A.9 Concentration of extract of trace elements after ICP-OES analysis – $C_{extract}$ (Lake Ngāpouri)

LAKE NGĀPOURI $C_{extract}$												
Depth (cm)	**Cd (ppm)**	**As (ppm)**	**Cu (ppm)**	**Zn (ppm)**	**P (ppm)**	**Pb (ppm)**	**Fe (ppm)**	**Mn (ppm)**	**Al (ppm)**	**Cr (ppm)**	**Ni (ppm)**	**V (ppm)**
1	0.0006u	0.9975	0.1307	7.2511	4.3252	0.0478	103.3993	11.0862	87.2730	0.0266	0.0404	0.0800
3	0.0182	0.8643	0.1285	6.0989	5.1372	0.0622	554.1108	11.2867	84.7060	0.0340	0.0545	0.1000
6	0.0184	0.9908	0.1107	2.2210	3.3761	0.0587	507.0409	10.7336	68.6650	0.0265	0.0578	0.0800
9	0.0231	0.8902	0.1062	2.5927	3.8696	0.0668	476.4421	10.9314	66.4860	0.0257	0.0535	0.0900
12	0.0190	1.3177	0.0977	1.4671	3.6291	0.0921	483.2819	11.2164	69.1700	0.0293	0.0350	0.1000
15	0.0169	1.1447	0.0842	1.1923	3.9798	0.0692	464.1833	10.7012	67.7360	0.0276	0.0262	0.1000
18	0.0114	0.5663	0.0710	0.6696	1.9112	0.0701	230.3532	10.9677	71.5670	0.0268	0.0143	0.1100
21	0.0091	2.4052	0.0647	1.0440	2.6894	0.0633	365.0277	10.4511	65.7730	0.0266	0.0208	0.1000
24	0.0247	1.9673	0.0546	1.0639	2.5306	0.0674	513.8438	11.4328	53.8590	0.0254	0.0191	0.0900
27	0.0456	1.5034	0.0554	1.6370	5.5087	0.0748	810.9742	10.9284	84.1640	0.0322	0.0302	0.1300
30	0.0282	0.9736	0.0586	1.4288	2.3341	0.0541	500.3632	10.8557	71.5050	0.0294	0.0230	0.1100
33	0.0327	1.3175	0.0481	1.2332	2.9991	0.0580	534.2429	11.1140	62.2750	0.0284	0.0246	0.1000
39	0.0308	1.8620	0.0657	1.4668	3.8127	0.0721	578.2817	10.5141	80.0870	0.0331	0.0324	0.1400
45	0.0282	1.4453	0.0531	1.2140	1.7625	0.0489	428.3652	10.4385	62.0560	0.0260	0.0246	0.1100
51	0.0269	1.5839	0.0604	1.1779	3.8529	0.0748	504.8947	16.6895	80.4100	0.0318	0.0198	0.1100
57	0.0620	1.8882	0.0486	1.5553	5.5098	0.0807	833.0700	11.9065	76.3330	0.0324	0.0192	0.1000
63	0.0504	2.1756	0.0544	1.4263	1.3880	0.0765	670.7858	11.0546	73.9730	0.0271	0.0320	0.0900
69	0.0906	1.9574	0.0468	1.7412	2.1351	0.0476	985.2863	10.4711	104.3540	0.0271	0.0319	0.0600
75	0.0846	0.7636	0.1455	2.0404	0.4825	0.2130	948.1271	10.9155	114.3540	0.0401	0.0515	0.0900
81	0.0559	2.0792	0.0804	0.5415	0.2828	0.1538	723.8126	10.5276	63.6480	0.0360	0.0178	0.1100
Blank1	-0.0020 u	-0.0016 u	0.0015 u	0.2295	#DIV/0!	0.0012 u	0.8291	10.4180	0.1410	-0.0001 u	-0.0014 u	0.00 u
Blank2	-0.0005 u	-0.0124 u	0.0019 u	0.0850	#DIV/0!	-0.0025 u	0.2974	10.9431	0.0740	0.0033	-0.0033 u	0.00 u

Table A. 10 concentration of extract of trace elements after ICP-OES analysis – $C_{extract}$ (Lake Forsyth)

LAKE FORSYTH– $C_{extract}$												
Depth cm	**Cd (ppm)**	**As (ppm)**	**Cu (ppm)**	**Zn (ppm)**	**P (ppm)**	**Pb (ppm)**	**Fe (ppm)**	**Mn (ppm)**	**Al (ppm)**	**Cr (ppm)**	**Ni (ppm)**	**V (ppm)**
1	0.0119	0.0327	0.0921	0.6702	12.7000	0.0723	258.6839	2.8816	95.2550	0.0950	0.0547	0.2400
3	0.0095	0.0458	0.1059	0.7047	8.0000	0.0684	241.4083	1.8964	113.8460	0.1035	0.0637	0.2700
6	0.0143	0.0383	0.1158	0.7334	7.0200	0.0859	272.1449	2.1225	144.8930	0.1180	0.0709	0.3100
9	0.0089	0.0494	0.0987	0.6495	6.2900	0.0655	259.1575	2.1317	121.3990	0.1095	0.0672	0.3000
12	0.0095	0.0390	0.0962	0.6091	5.5600	0.0494	245.1042	2.2245	116.6080	0.1021	0.0576	0.2500
15	0.0174	0.0381	0.0822	0.5113	4.6400	0.0503	296.8609	2.2141	103.1900	0.0959	0.0595	0.2300
18	0.0127	0.0498	0.0896	0.5812	5.2400	0.0404	328.3756	2.4949	111.1560	0.1067	0.0563	0.2500
21	0.0097	0.0374	0.0821	0.5387	4.9600	0.0383	249.6674	2.3865	120.6410	0.1037	0.0613	0.2600
24	0.0145	0.0467	0.0774	0.5302	4.3300	0.0336	223.1733	2.1972	100.4340	0.0852	0.0506	0.2200
27	0.0139	0.0203	0.0709	0.5890	5.4400	0.0465	322.9046	3.1177	113.3370	0.1333	0.0850	0.2800
30	0.0137	0.0183	0.0680	0.5625	4.9800	0.0468	286.1423	3.0869	88.3900	0.1161	0.0720	0.2500
33	0.0140	0.0328	0.0767	0.6079	5.7500	0.0342	328.0454	3.4357	118.9740	0.1377	0.0883	0.2800
36	0.0185	0.0137	0.0746	0.6118	5.6800	0.0509	328.7439	3.6688	100.4830	0.1239	0.0840	0.2700
39	0.0125	0.0218	0.0820	0.5864	5.8100	0.0536	327.0294	3.8301	102.1650	0.1255	0.0761	0.2700
42	0.0222	0.0135	0.0894	0.7052	6.3700	0.0468	408.4264	4.6665	97.8360	0.1296	0.0932	0.2900
45	0.0199	0.0180	0.0832	0.6286	5.9500	0.0545	410.5170	4.7683	91.1260	0.1223	0.0830	0.2700
48	0.0178	0.0348	0.0918	0.6454	6.4700	0.0669	360.5652	5.0363	105.1590	0.1307	0.0879	0.3000
51	0.0196	0.0367	0.0854	0.6103	6.3900	0.0628	415.3217	4.9764	96.2140	0.1284	0.0839	0.2800
54	0.0096	0.0219	0.0904	0.6182	6.4400	0.0496	327.6240	5.3176	106.7850	0.1281	0.0886	0.2900
60	0.0155	0.0191	0.0937	0.6288	6.2300	0.0720	384.0637	4.7388	125.4170	0.1427	0.0956	0.3000
66	0.0227	0.0191	0.0939	0.6200	6.4500	0.0652	397.8916	4.6014	109.4120	0.1302	0.0863	0.2800
72	0.0189	0.0278	0.0962	0.6293	6.6800	0.0719	370.6087	5.2794	116.2040	0.1367	0.0923	0.3000
78	0.0198	0.0256	0.0938	0.6455	6.7300	0.0648	391.8120	5.1092	121.4460	0.1391	0.0990	0.3000
84	0.0223	0.0219	0.1095	0.7045	7.1700	0.0794	401.9819	5.5477	158.3660	0.1591	0.1117	0.3400
BLK1	-0.0018 u	-0.0030 u	-0.0010 u	0.1188	0.0300	0.0000 u	0.5837	0.0083	0.4860	0.0020	-0.0007 u	0.00 u

BLK2	-0.0019 u	-0.0158 u	-0.0019 u	0.0141	0.00 u	-0.0035 u	-0.0787 u	0.0002 u	0.0850	0.0018	0.0017 u	0.00 u
BLK3	0.0001 u	-0.0022 u	-0.0013 u	0.0220	0.00 u	-0.0027 u	-0.1578 u	-0.0006 u	0.0530	0.0017	-0.0042 u	0.00 u

Table A.11 Concentration of extract of trace elements after ICP-OES analysis – $C_{extract}$ for F10 and F10 cores collected from Lake Forsyth by previous student as described in section 3.3.6 of chapter 3.

LAKE FORSYTH PREVIOUS CORE												
	F10 core						**F11 core**					
Depth cm	**Cd (ppm)**	**As (ppm)**	**Cu (ppm)**	**Zn (ppm)**	**P (ppm)**	**Pb (ppm)**	**Cd (ppm)**	**As (ppm)**	**Cu (ppm)**	**Zn (ppm)**	**P (ppm)**	**Pb (ppm)**
1	0.1107	0.0562	0.1661	0.869	18.7041	0.1741	0.023	0.0169	0.0373	0.3873	5.1914	0.0581
2	0.0144	0.0333	0.0972	0.7005	10.5683	0.1124	0.0063	0.0197	0.0381	0.3736	5.0539	0.0595
3	0.0128	0.0298	0.0893	0.5975	10.4838	0.1191	0.0061	0.0085	0.0326	0.3437	4.4206	0.0545
4	0.0125	0.0368	0.096	0.5921	9.6282	0.1223	0.0068	0.0176	0.0435	0.3948	4.9027	0.0653
5	0.0185	0.0368	0.0951	0.5737	9.2401	0.1197	0.0072	0.0094	0.0378	0.3672	4.3847	0.0607
7	0.0113	0.0343	0.0786	0.4909	6.4761	0.0957	0.0077	0.0212	0.0526	0.4331	4.9429	0.075
9	0.0137	0.0442	0.1059	0.6909	6.6331	0.1194	0.0065	0.0193	0.0351	0.3546	4.2071	0.0601
11	0.0151	0.0421	0.1238	0.7244	7.2795	0.1365	0.0072	0.026	0.0481	0.4186	4.7217	0.0715
13	0.0178	0.0522	0.1356	0.75	8.0556	0.1561	0.008	0.0219	0.0463	0.4102	4.6778	0.0729
15	0.0162	0.0448	0.1351	0.7139	7.7893	0.1511	0.0082	0.0226	0.054	0.4341	4.978	0.0763
20	0.0162	0.0489	0.1286	0.705	7.5652	0.1443	0.0089	0.0246	0.0464	0.3677	3.7036	0.049
25	0.0193	0.044	0.1176	0.6439	7.0824	0.136	0.0068	0.0139	0.047	0.3683	3.7654	0.0477
Blank	0.0029	0.002	0.0023	0.0362	0.0574	0.0034	0.0000 u	-0.0020 u	0.0003	0.0023	0.0010 u	0.0000 u

Table A. 12 Table Concentration of extract of trace elements after ICP-OES analysis – $C_{extract}$ (Lake Pearson)

LAKE PEARSON - $C_{extract}$												
Depth cm	**Cd (ppm)**	**As (ppm)**	**Cu (ppm)**	**Zn (ppm)**	**P (ppm)**	**Pb (ppm)**	**Fe (ppm)**	**Mn (ppm)**	**Al (ppm)**	**Cr (ppm)**	**Ni (ppm)**	**V (ppm)**
1	0.0662	0.1595	0.2812	1.3085	11.09	0.3993	445.4555	9.7508	329.016	0.2196	0.2099	0.53
3	0.0716	0.1859	0.3001	1.358	11.59	0.4156	475.1328	10.0236	383.491	0.2381	0.2304	0.50
6	0.0696	0.1719	0.2847	1.3379	11.64	0.3959	453.3486	9.3249	365.686	0.2166	0.2152	0.47
9	0.0654	0.1934	0.2719	1.3612	12.75	0.3741	442.4918	8.9973	373.342	0.2141	0.2053	0.48
12	0.0648	0.2	0.3457	1.5442	12.17	0.4189	462.9819	9.5662	449.313	0.3176	0.2336	0.48
15	0.0716	0.2129	0.3856	1.5258	11.01	0.4382	469.7597	9.0188	404.063	0.3069	0.2465	0.49
18	0.0733	0.1857	0.3484	1.5159	9.9	0.4296	476.4738	8.6542	413.694	0.3372	0.2333	0.57
21	0.0878	0.1475	0.2579	1.4451	13.25	0.391	527.369	10.8703	382.967	0.3116	0.2005	0.56
24	0.1046	0.1895	0.2689	1.5643	20.45	0.4103	614.5989	13.8496	412.526	0.3348	0.2123	0.61
27	0.0603	0.1212	0.2767	1.3608	8.05	0.3712	391.3762	8.004	398.564	0.2951	0.1947	0.51
30	0.0547	0.1395	0.3121	1.3063	6.84	0.3596	381.1004	6.9535	346.38	0.2753	0.2052	0.47
33	0.0596	0.1524	0.4144	1.6138	7.16	0.4349	399.635	7.2359	377.227	0.3063	0.2422	0.51
36	0.0685	0.1634	0.4605	1.7607	7.18	0.47	428.7876	8.0692	393.743	0.31	0.2561	0.51
39	0.0603	0.0924	0.3733	1.4599	8.2	0.4441	374.5141	6.4272	320.38	0.2783	0.2661	0.41
42	0.069	0.1248	0.5112	1.9672	8.65	0.556	429.7531	7.933	403.833	0.3311	0.3166	0.48
48	0.055	0.081	0.3973	1.546	7.67	0.4312	357.2325	6.7686	329.698	0.2734	0.2517	0.41
54	0.0529	0.0891	0.3904	1.4443	7.84	0.4425	344.289	6.6303	354.113	0.2572	0.2015	0.39
60	0.0128	0.1812	0.5323	1.6122	8.35	0.3316	375.7786	6.6291	165.263	0.2419	0.1601	0.41
66	0.0151	0.1608	0.5471	1.701	8.1	0.3437	382.8253	6.565	167.77	0.2579	0.196	0.41
72	0.0204	0.1633	0.5691	1.8231	9	0.3788	441.7123	8.0461	182.043	0.2744	0.2116	0.46
78	0.0197	0.225	0.5445	1.6777	8.46	0.3518	443.6198	8.7175	171.619	0.2603	0.2002	0.43
84	0.0235	0.1756	0.5507	1.7267	9.39	0.3743	446.5842	8.1171	179.858	0.2742	0.2174	0.42
BLK	0.0004 u	0.0355		0.1149	0.03	-0.0066 u	0.3972	0.005	-0.021 u	0.0008 u	0.0052	0

Table A. 13 Concentration of extract of trace elements after ICP-OES analysis – $C_{extract}$ (Lake Heron)

LAKE HERON – $C_{extract}$												
Depth cm	**Cd (ppm)**	**As (ppm)**	**Cu (ppm)**	**Zn (ppm)**	**P (ppm)**	**Pb (ppm)**	**Fe (ppm)**	**Mn (ppm)**	**Al (ppm)**	**Cr (ppm)**	**Ni (ppm)**	**V (ppm)**
1	0.0297	0.2694	0.1915	1.0006	20.23	0.2346	435.2519	17.9868	150.012	0.2630	0.1820	0.39
3	0.0267	0.1680	0.1745	0.9794	12.79	0.2352	387.4017	13.8230	142.948	0.2363	0.1644	0.35
6	0.0216	0.1323	0.1911	0.9697	8.92	0.2366	379.7239	11.7277	157.01	0.2623	0.1831	0.38
9	0.0243	0.1550	0.2107	1.3808	14.7	0.2458	409.4787	15.6170	162.993	0.2588	0.1844	0.38
12	0.0193	0.1335	0.1730	0.9259	10.25	0.2101	360.1767	12.2580	134.009	0.2406	0.1719	0.35
15	0.0264	0.1503	0.1715	0.9604	14.37	0.2191	382.2293	14.8285	138.594	0.2421	0.1690	0.36
18	0.0201	0.1241	0.1768	0.9553	10.37	0.2210	342.3558	11.2644	131.551	0.2336	0.1674	0.35
21	0.0257	0.1290	0.1988	1.0263	10.71	0.2470	408.4849	11.8065	174.586	0.2603	0.1871	0.38
24	0.0219	0.1238	0.2245	1.7771	9.72	0.2438	369.8864	9.6732	156.772	0.2439	0.1814	0.35
27	0.0192	0.1342	0.2219	1.1641	10.43	0.2513	366.9988	10.9040	146.538	0.2522	0.1912	0.41
30	0.0246	0.1334	0.2261	1.1239	11.55	0.2624	386.9537	10.4812	146.541	0.2630	0.1964	0.42
36	0.0206	0.1194	0.1996	1.0806	8.66	0.2088	346.0085	9.1514	132.13	0.2391	0.1738	0.37
42	0.0255	0.2111	0.1821	0.9253	12.24	0.1982	390.0174	10.2061	124.644	0.2279	0.1523	0.35
48	0.0251	0.2005	0.1969	1.0104	10.68	0.2023	407.2278	10.2507	136.106	0.2563	0.1683	0.39
54	0.0246	0.1113	0.1988	1.0601	8.83	0.2144	360.0493	8.1479	161.874	0.2951	0.2040	0.41
60	0.0165	0.0670	0.1742	0.9594	7.95	0.1753	289.8946	5.7201	147.897	0.2552	0.1688	0.35
66	0.0189	0.0974	0.2002	1.0390	8.38	0.1951	326.6606	6.6384	183.51	0.2803	0.2017	0.37
72	0.0210	0.0987	0.2119	1.2230	8.70	0.2168	341.3514	7.1485	188.302	0.2885	0.2037	0.39
78	0.0227	0.1329	0.2315	1.1377	9.74	0.2449	395.4787	8.7443	176.334	0.2828	0.1990	0.42
84	0.0152	0.0931	0.1145	0.6468	6.43	0.1170	216.0683	5.0990	91.761	0.1402	0.0964	0.21
BK1	-0.0003 u	0.0000 u	0.0010 u	0.0931	0.03	-0.0026 u	0.5797	0.0076	0.9230	0.0013	-0.0098 u	0.00 u

Table A.14 Concentration of extract of trace elements after ICP-OES analysis – $C_{extract}$ (Lake Moawhitu)

LAKE MOAWHITU – $C_{extract}$												
Depth cm	**Cd (ppm)**	**As (ppm)**	**Cu (ppm)**	**Zn (ppm)**	**P (ppm)**	**Pb (ppm)**	**Fe (ppm)**	**Mn (ppm)**	**Al (ppm)**	**Cr (ppm)**	**Ni (ppm)**	**V (ppm)**
1	0.0709	0.0355	0.71480	0.8933	8.42	0.0538	485.7331	6.3700	384.307	1.7086	0.7293	1.33
3	0.0750	0.0367	0.7073	1.1745	10.95	0.0555	491.0996	6.0340	365.342	1.6221	0.7134	1.30
6	0.0826	0.0456	0.7263	0.9961	8.27	0.0597	545.6159	7.1988	407.415	1.8666	0.7780	1.37
9	0.0735	0.0387	0.6440	0.8384	7.46	0.0510	484.1677	6.1197	360.082	1.6288	0.6892	1.27
12	0.0684	0.0361	0.5777	0.7551	6.64	0.0506	438.1315	5.6486	336.108	1.4911	0.6465	1.14
15	0.0733	0.0430	0.6102	0.8343	7.64	0.0532	452.4447	6.0050	335.577	1.5459	0.6879	1.18
18	0.0697	0.0573	0.6040	0.7475	8.37	0.0504	446.1215	5.6794	334.496	1.596	0.7436	1.21
21	0.0655	0.0514	0.5845	0.6804	8.11	0.0535	428.2949	5.3376	304.278	1.484	0.6851	1.15
24	0.0753	0.0509	0.6284	0.7883	10.04	0.0567	459.4385	5.8535	337.32	1.6858	0.8354	1.20
27	0.0697	0.0710	0.5903	0.6838	8.41	0.0595	440.8229	4.6546	291.975	1.6514	0.9252	1.13
30	0.0754	0.0708	0.5577	0.7976	8.18	0.0520	457.0200	4.6453	306.995	1.8072	1.0262	1.15
33	0.0507	0.0470	0.4127	0.5159	5.94	0.0353	342.2391	3.2492	237.321	1.3114	0.7620	0.84
39	0.0666	0.0508	0.5007	0.7425	6.90	0.0501	426.711	3.9963	321.185	1.4982	0.7765	1.10
45	0.0722	0.0481	0.4879	0.7776	7.21	0.0580	479.4726	4.3152	375.760	1.6791	0.7989	1.15
51	0.0666	0.0326	0.4556	0.7891	6.35	0.0517	419.5308	3.6722	355.643	1.5291	0.6888	0.99
57	0.0655	0.0262	0.4381	0.8230	12.55	0.0288	443.1493	3.8678	251.833	1.7551	0.7423	0.95
63	0.0522	0.0366	0.4062	0.6574	7.44	0.0394	400.1140	3.6072	264.869	1.4896	0.7070	0.92
69	0.0601	0.0357	0.4865	0.7302	5.73	0.0373	464.3138	3.6822	264.983	1.8641	0.7843	1.05
75	0.0611	0.0202	0.4482	0.6400	5.81	0.0228	438.7941	3.6759	235.920	1.6846	0.7115	0.95
81	0.0711	0.0255	0.4444	0.6437	5.69	0.0412	458.6345	3.3296	242.514	1.8685	0.7910	1.00
BLK	0.0005 u	-0.0034 u	0.0020	0.0907	0.03	-0.0037 u	0.7566	0.0063	0.3690	-0.1036 u	0.0004 u	0.00
BLK2	0.0013	-0.0012 u	0.0008 u	0.0363	0.02	-0.0080 u	0.0452	0.0026	0.5510	-0.1078 u	-0.0005 u	0.00 u

A.3 Concentration of trace elements in sediments

This section presents the concentration of trace elements in sediments as described in section 3.3.4 and as calculated using equation 2.

Table A.15 Concentration of trace elements in dry sediments for Lake Tutaeinanga

LAKE TUTAEINANGA ($C_{sediments}$)												
Depth cm	**Cd (mg/kg)**	**As (mg/kg)**	**Cu (mg/kg)**	**Zn (mg/kg)**	**P (g/kg)**	**Pb (mg/kg)**	**Fe (g/kg)**	**Mn (g/kg)**	**Al (g/kg)**	**Cr (mg/kg)**	**Ni (mg/kg)**	**V (mg/kg)**
1	1.7462	31.9863	35.6836	235.6946	3.6563	19.9072	20.3137	0.2732	17.6115	7.4908	6.8525	154.1511
2	1.2662	33.3091	42.3722	184.9936	2.3080	16.9489	22.6972	0.1923	13.5220	4.6315	5.9421	148.8301
3	1.6361	26.5419	41.5938	176.1732	2.2064	15.0893	19.1502	0.1804	15.8102	4.5997	4.9550	139.3006
4	0.9990	21.6615	59.6125	145.6061	1.6126	16.4933	13.0681	0.1810	15.5986	4.3731	13.2619	156.9822
5	1.1195	23.8119	36.9834	156.6661	1.8935	18.4187	13.0900	0.2219	17.9162	4.8773	4.0108	174.2573
6	0.9334	22.2751	22.5615	137.9145	1.7014	14.9773	11.2649	0.2232	18.6788	4.8263	3.1928	151.6826
7	1.0575	21.9749	26.3741	132.6422	1.9257	17.1844	10.9255	0.2602	20.7155	5.3510	2.9927	161.7975
8	1.2390	27.9129	24.6455	162.4001	2.4366	20.6978	13.6169	0.3237	24.9695	6.6442	4.1906	196.7750
9	0.9370	22.0309	16.7627	129.1765	1.5513	14.4513	11.7772	0.2118	17.0812	4.2479	3.3005	154.0915
10	0.8005	17.7205	16.9748	107.6718	1.2753	16.1195	9.7793	0.2233	17.8282	4.9674	3.3665	173.2574
11	0.6651	20.7020	14.1755	84.9488	1.0798	13.5519	10.2987	0.1932	15.6830	3.5127	2.5877	147.5743
12	0.7884	17.4627	12.5322	124.6039	1.4344	13.3441	9.1833	0.2907	21.6758	5.0129	2.3888	170.6259
13	0.4472	14.4649	9.6502	68.2273	0.7373	8.9327	7.7538	0.1491	12.1187	2.6101	1.6118	109.1886
14	0.5821	15.0777	8.9942	70.5468	1.0120	9.8674	8.1670	0.2011	16.7257	3.4444	1.5136	143.5969
15	0.6065	13.1170	9.2729	68.0499	1.1591	10.3195	8.1337	0.2238	17.5776	3.8930	1.7118	137.9191
16	0.6576	15.1336	11.0942	84.7521	1.2278	11.2633	8.9992	0.2318	19.3613	3.8327	2.0855	154.0607
17	0.5749	14.4753	9.4900	70.5574	1.1283	10.2708	8.8067	0.2217	17.8342	7.8254	1.5187	147.5844
18	0.6965	29.0769	19.8686	111.0541	1.1369	14.7804	11.7779	0.2188	17.6544	4.4152	3.0104	165.2766
19	0.5387	16.0720	9.7869	83.0423	1.1167	11.3245	8.4701	0.2478	17.1677	3.7823	1.7621	161.6178
20	0.3616	16.8325	8.3834	59.4617	0.8920	10.0491	8.1958	0.2153	15.0060	3.5287	1.5342	158.9006
21	0.4540	18.1107	8.5297	72.0724	0.8207	10.3097	7.8580	0.2285	14.4760	3.9184	1.3858	155.3026

22	0.4392	17.9431	10.9371	139.8109	0.8521	10.8383	8.4675	0.2264	16.3252	3.7885	1.3177	164.7159
23	0.3541	17.0804	8.1312	125.4721	0.8107	9.9137	7.0882	0.2154	14.6149	3.4796	1.2087	151.3918
24	0.3620	14.6923	5.4085	77.2517	0.4695	6.9948	7.4901	0.1739	11.4297	3.0556	0.8730	208.6733
25	0.2892	31.1324	7.6746	109.2010	0.6735	9.9884	11.4172	0.2533	12.8897	4.2660	1.3325	277.8574
26	0.2057	12.9794	5.3477	57.2221	0.4925	7.3611	7.1233	0.1848	9.5799	3.1826	0.8985	171.0384
27	0.1486	9.8860	5.0173	72.9961	0.4526	7.1430	6.2657	0.1826	9.9517	3.3029	0.5943	132.5747
28	0.1479	6.5196	4.9663	36.4757	0.4258	7.0690	5.9817	0.1749	9.8637	3.2228	0.3276	119.4019
29	0.2135	7.0898	4.8262	54.1876	0.4025	7.3247	6.9983	0.1725	11.5820	3.1391	0.4912	137.7379
30	0.1936	6.6776	4.6130	50.0550	0.3850	7.1937	6.4491	0.1719	11.2275	3.1291	0.4946	134.4118
33	0.1669	10.7376	5.0406	55.4239	0.3872	7.5108	7.7276	0.1899	13.9667	3.8277	0.7678	176.9204
36	0.1843	13.1409	5.8874	43.2825	0.3914	8.3811	8.0301	0.1980	15.9900	4.1092	0.7698	209.2567
39	0.1920	11.0138	5.7950	84.1681	0.3332	8.2462	7.7783	0.1675	13.2889	4.1118	1.3330	236.0910
42	0.5741	22.7531	4.9326	74.2582	0.3445	6.9829	9.2611	0.1658	12.5242	3.7258	1.2888	251.9014
45	0.2990	30.1513	5.2042	75.4724	0.3366	6.6326	12.1927	0.1490	11.5167	3.3440	1.1848	235.8512
48	0.2546	23.4056	6.4327	88.3964	0.2546	9.0566	9.2646	0.1322	14.2354	3.4654	0.9632	178.2542
51	0.4921	51.5566	7.6433	139.2520	0.3597	9.1413	16.6226	0.1359	12.7158	4.9315	1.9682	212.1310
54	0.4018	28.5845	10.9047	183.3157	0.4956	12.3446	12.3080	0.1755	18.2417	4.3865	1.4063	315.8692
57	0.3841	15.2025	9.4172	76.8041	0.4132	13.6660	7.0850	0.1873	21.5894	4.8192	1.5482	251.4349
26 repeat	0.7914	24.3125	17.1799	232.4888	1.2933	15.8673	12.2852	0.2606	21.3326	4.5845	2.8665	177.5902

Table A.16 Concentration of trace elements in dry sediments for Lake Ngāpouri

Lake Ngāpouri ($C_{sediments}$)												
Depth (cm)	**Cd (mg/kg)**	**As (mg/kg)**	**Cu (mg/kg)**	**Zn (mg/kg)**	**P(g/kg)**	**Pb (mg/kg)**	**Fe (g/kg)**	**Mn (g/kg)**	**Al (g/kg)**	**Cr (mg/kg)**	**Ni (mg/kg)**	**V (mg/kg)**
1	-	107.8877	14.1363	784.2648	4.3252	5.1700	11.1835	0.1747	9.4393	2.8770	4.3696	8.6526
3	1.9270	91.5112	13.6054	645.7454	5.1372	6.5857	58.6687	0.7907	8.9686	3.5999	5.7704	10.5879
6	1.8287	98.4708	11.0019	220.7345	3.3761	5.8339	50.3924	0.7962	6.8243	2.6337	5.7445	7.9508
9	2.4003	92.5013	11.0353	269.4091	3.8696	6.9412	49.5074	0.9302	6.9086	2.6705	5.5592	9.3520
12	2.0239	140.3595	10.4069	156.2733	3.6291	9.8104	51.4785	0.9198	7.3679	3.1210	3.7281	10.6519
15	1.6234	109.9611	8.0883	114.5336	3.9798	6.6474	44.5899	0.6916	6.5068	2.6513	2.5168	9.6061
18	1.2429	61.7396	7.7406	73.0017	1.9112	7.6425	25.1138	0.4918	7.8024	2.9218	1.5590	11.9925
21	0.8560	226.2555	6.0863	98.2084	2.6894	5.9546	34.3379	0.6917	6.1872	2.5022	1.9566	9.4069
24	2.7523	219.2178	6.0841	118.5512	2.5306	7.5104	57.2580	0.7893	6.0016	2.8303	2.1283	10.0288
27	4.6142	152.1274	5.6059	165.6462	5.5087	7.5689	82.0616	0.9589	8.5165	3.2583	3.0559	13.1546
30	2.9837	103.0128	6.2002	151.1757	2.3341	5.7241	52.9415	0.3801	7.5657	3.1107	2.4335	11.6387
33	3.3009	132.9945	4.8554	124.4849	2.9991	5.8548	53.9289	0.4218	6.2863	2.8668	2.4832	10.0945
39	2.9737	179.7728	6.3432	141.6169	3.8127	6.9611	55.8321	0.4870	7.7323	3.1957	3.1282	13.5167
45	2.8304	145.0650	5.3297	121.8494	1.7625	4.9081	42.9951	0.4048	6.2286	2.6096	2.4691	11.0407
51	3.9695	233.7268	8.9129	173.8158	3.8529	11.0378	74.5043	0.7200	11.8656	4.6925	2.9218	16.2321
57	6.5155	198.4277	5.1073	163.4438	5.5098	8.4806	87.5459	0.9727	8.0217	3.4049	2.0177	10.5088
63	4.9969	215.6985	5.3935	141.4097	1.3880	7.5845	66.5047	0.3885	7.3340	2.6868	3.1726	8.9230
69	8.4103	181.7033	4.3444	161.6337	2.1351	4.4187	91.4630	0.5642	9.6871	2.5157	2.9612	5.5697
75	8.2970	74.8884	14.2696	200.1077	0.4825	20.8895	92.9855	0.2207	11.2150	3.9327	5.0507	8.8265
81	5.6261	209.2637	8.0920	54.5000	0.2828	15.4794	72.8490	0.3272	6.4059	3.6233	1.7915	11.0711

Table A. 17 Concentration of trace elements in dry sediments for Lake Forsyth

LAKE FORSYTH ($C_{sediments}$)												
Depth (cm)	**Cd (mg/kg)**	**As (mg/kg)**	**Cu (mg/kg)**	**Zn (mg/kg)**	**P(g/kg)**	**Pb (mg/kg)**	**Fe (g/kg)**	**Mn (g/kg)**	**Al (g/kg)**	**Cr (mg/kg)**	**Ni (mg/kg)**	**V (mg/kg)**
1	1.2739	3.5006	9.8595	71.7466	1.3596	7.7399	27.6928	0.3085	10.1973	10.1700	5.8558	25.6926
3	0.9419	4.5411	10.5000	69.8709	0.7932	6.7819	23.9356	0.1880	11.2878	10.2620	6.3158	26.7705
6	1.3077	3.5025	10.5898	67.0686	0.6420	7.8555	24.8874	0.1941	13.2503	10.7910	6.4837	28.3492
9	0.8376	4.6491	9.2889	61.1260	0.5920	6.1644	24.3899	0.2006	11.4251	10.3053	6.3243	28.2337
12	0.9838	4.0389	9.9627	63.0796	0.5758	5.1160	25.3835	0.2304	12.0762	10.5737	5.9652	25.8905
15	1.6936	3.7085	8.0010	49.7676	0.4516	4.8960	28.8951	0.2155	10.0440	9.3345	5.7915	22.3872
18	1.1900	4.6663	8.3955	54.4584	0.4910	3.7855	30.7688	0.2338	10.4153	9.9978	5.2753	23.4250
21	1.0324	3.9807	8.7383	57.3363	0.5279	4.0764	26.5733	0.2540	12.8404	11.0373	6.5244	27.6730
24	1.6546	5.3290	8.8322	60.5017	0.4941	3.8341	25.4665	0.2507	11.4606	9.7223	5.7740	25.1044
27	1.3615	1.9884	6.9446	57.6917	0.5328	4.5546	31.6280	0.3054	11.1012	13.0565	8.3256	27.4256
30	1.4562	1.9451	7.2277	59.7880	0.5293	4.9744	30.4140	0.3281	9.3950	12.3402	7.6529	26.5725
33	1.3947	3.2676	7.6411	60.5610	0.5728	3.4071	32.6810	0.3423	11.8526	13.7181	8.7967	27.8945
36	1.8311	1.3560	7.3839	60.5563	0.5622	5.0381	32.5392	0.3631	9.9459	12.2637	8.3144	26.7247
39	1.3156	2.2944	8.6303	61.7169	0.6115	5.6412	34.4189	0.4031	10.7526	13.2085	8.0093	28.4167
42	2.2526	1.3698	9.0713	71.5559	0.6464	4.7487	41.4426	0.4735	9.9273	13.1504	9.4569	29.4260
45	2.0145	1.8222	8.4225	63.6343	0.6023	5.5171	41.5574	0.4827	9.2248	12.3806	8.4022	27.3326
48	1.7977	3.5145	9.2711	65.1805	0.6534	6.7564	36.4143	0.5086	10.6203	13.1997	8.8772	30.2977
51	1.8769	3.5144	8.1780	58.4427	0.6119	6.0138	39.7714	0.4765	9.2135	12.2957	8.0343	26.8130
54	0.9262	2.1129	8.7217	59.6432	0.6213	4.7854	31.6088	0.5130	10.3025	12.3589	8.5480	27.9789
60	1.5641	1.9274	9.4554	63.4528	0.6287	7.2656	38.7562	0.4782	12.6559	14.4000	9.6471	30.2733
66	2.4731	2.0809	10.2302	67.5478	0.7027	7.1034	43.3495	0.5013	11.9202	14.1850	9.4022	30.5055
72	1.8461	2.7154	9.3964	61.4672	0.6525	7.0229	36.1994	0.5157	11.3503	13.3522	9.0154	29.3026
78	1.9493	2.5203	9.2347	63.5498	0.6626	6.3796	38.5741	0.5030	11.9564	13.6945	9.7466	29.5351
84	2.1580	2.1193	10.5964	68.1748	0.6938	7.6836	38.9000	0.5369	15.3252	15.3962	10.8093	32.9020

Table A.18 Concentration of trace elements in dry sediments of Lake Pearson

LAKE PEARSON ($C_{sediments}$)												
Depth (cm)	**Cd (mg/kg)**	**As (mg/kg)**	**Cu (mg/kg)**	**Zn (mg/kg)**	**P (g/kg)**	**Pb (mg/kg)**	**Fe (g/kg)**	**Mn (g/kg)**	**Al (g/kg)**	**Cr (mg/kg)**	**Ni (mg/kg)**	**V (mg/kg)**
1	6.8279	16.4509	29.0030	134.9589	1.1438	41.1839	45.9444	1.0057	33.9348	22.6496	21.6491	54.6643
3	7.1270	18.5043	29.8716	135.1738	1.1537	41.3684	47.2942	0.9977	38.1723	23.7002	22.9338	49.7694
6	7.3157	18.0685	29.9249	140.6273	1.2235	41.6132	47.6517	0.9801	38.4374	22.7669	22.6198	49.4019
9	6.8617	20.2912	28.5273	142.8151	1.3377	39.2500	46.4256	0.9440	39.1705	22.4631	21.5398	50.3609
12	6.4793	19.9978	34.5661	154.4026	1.2169	41.8853	46.2930	0.9565	44.9262	31.7564	23.3574	47.9946
15	7.5008	22.3033	40.3952	159.8419	1.1534	45.9056	49.2117	0.9448	42.3294	32.1507	25.8232	51.3321
18	7.9007	20.0159	37.5528	163.3935	1.0671	46.3051	51.3574	0.9328	44.5906	36.3456	25.1466	61.4383
21	9.4361	15.8522	27.7172	155.3089	1.4240	42.0219	56.6778	1.1683	41.1585	33.4885	21.5483	60.1848
24	11.0943	20.0992	28.5207	165.9162	2.1690	43.5181	65.1869	1.4689	43.7542	35.5103	22.5174	64.6991
27	6.8759	13.8202	31.5516	155.1695	0.9179	42.3272	44.6279	0.9127	45.4475	33.6497	22.2013	58.1543
30	5.4148	13.8093	30.8953	129.3127	0.6771	35.5974	37.7257	0.6883	34.2887	27.2524	20.3131	46.5260
33	6.4692	16.5420	44.9804	175.1674	0.7772	47.2055	43.3778	0.7854	40.9455	33.2469	26.2892	55.3572
36	6.9162	16.4980	46.4954	177.7728	0.7249	47.4545	43.2934	0.8147	39.7551	31.2998	25.8577	51.4932
39	7.0175	10.7532	43.4433	169.8980	0.9543	51.6828	43.5846	0.7480	37.2847	32.3876	30.9678	47.7144
42	7.2235	13.0651	53.5167	205.9428	0.9056	58.2067	44.9901	0.8305	42.2766	34.6623	33.1443	50.2504
48	5.6458	8.3147	40.7829	158.6973	0.7873	44.2628	36.6700	0.6948	33.8436	28.0646	25.8371	42.0866
54	5.7838	9.7417	42.6843	157.9124	0.8572	48.3807	37.6428	0.7249	38.7169	28.1209	22.0310	42.6406
60	1.2712	17.9948	52.8621	160.1058	0.8292	32.9308	37.3181	0.6583	16.4121	24.0228	15.8993	40.7166
66	1.5382	16.3798	55.7300	173.2714	0.8251	35.0108	38.9963	0.6687	17.0898	26.2708	19.9654	41.7644
72	1.9979	15.9933	55.7366	178.5509	0.8814	37.0989	43.2605	0.7880	17.8289	26.8742	20.7237	45.0515
78	2.0572	23.4956	56.8593	175.1935	0.8834	36.7366	46.3249	0.9103	17.9213	27.1818	20.9058	44.9027
84	2.2952	17.1503	53.7852	168.6416	0.9171	36.5568	43.6165	0.7928	17.5662	26.7803	21.2328	41.0201

Table A. 19 Concentration of trace elements in dry sediments of Lake Heron

LAKE HERON ($C_{sediments}$)												
Depth (cm)	**Cd (mg/kg)**	**As (mg/kg)**	**Cu (mg/kg)**	**Zn (mg/kg)**	**P(g/kg)**	**Pb (mg/kg)**	**Fe (g/kg)**	**Mn (g/kg)**	**Al (g/kg)**	**Cr (mg/kg)**	**Ni (mg/kg)**	**V (mg/kg)**
1	3.1482	28.5567	20.2992	106.0646	2.1444	24.8678	46.1371	1.9066	15.9014	27.8783	19.2922	41.3404
3	2.8433	17.8907	18.5829	104.2986	1.3620	25.0470	41.2553	1.4720	15.2229	25.1641	17.5073	37.2723
6	2.2357	13.6935	19.7795	100.3672	0.9232	24.4889	39.3027	1.2139	16.2517	27.1489	18.9515	39.3313
9	2.4860	15.8574	21.5558	141.2637	1.5039	25.1467	41.8920	1.5977	16.6751	26.4767	18.8652	38.8762
12	2.0711	14.3263	18.5652	99.3614	1.1000	22.5465	38.6518	1.3154	14.3810	25.8196	18.4472	37.5597
15	2.7351	15.5711	17.7675	99.4978	1.4887	22.6988	39.5991	1.5362	14.3584	25.0817	17.5085	37.2961
18	2.0811	12.8489	18.3053	98.9086	1.0737	22.8816	35.4464	1.1663	13.6204	24.1862	17.3320	36.2379
21	2.6663	13.3834	20.6250	106.4760	1.1111	25.6256	42.3792	1.2249	18.1128	27.0055	19.4111	39.4240
24	2.3261	13.1492	23.8449	188.7520	1.0324	25.8949	39.2869	1.0274	16.6513	25.9055	19.2671	37.1747
27	2.0169	14.0976	23.3105	122.2880	1.0957	26.3989	38.5530	1.1455	15.3937	26.4935	20.0854	43.0703
30	2.4714	13.4016	22.7144	112.9091	1.1603	26.3612	38.8741	1.0530	14.7218	26.4215	19.7307	42.1940
36	2.2549	13.0694	21.8480	118.2813	0.9479	22.8550	37.8737	1.0017	14.4628	26.1716	19.0240	40.4998
42	2.7221	22.5351	19.4393	98.7765	1.3066	21.1580	41.6346	1.0895	13.3058	24.3285	16.2581	37.3628
48	2.4141	19.2838	18.9376	97.1790	1.0272	19.4570	39.1666	0.9859	13.0905	24.6506	16.1869	37.5097
54	2.2839	10.3334	18.4572	98.4230	0.8198	19.9056	33.4281	0.7565	15.0289	27.3980	18.9400	38.0657
60	1.7830	7.2402	18.8244	103.6747	0.8591	18.9433	31.3266	0.6181	15.9821	27.5774	18.2409	37.8217
66	2.0075	10.3456	21.2647	110.3596	0.8901	20.7230	34.6970	0.7051	19.4919	29.7727	21.4240	39.3004
72	2.0331	9.5556	20.5151	118.4049	0.8423	20.9895	33.0480	0.6921	18.2305	27.9312	19.7212	37.7579
78	2.2704	13.2925	23.1543	113.7910	0.9742	24.4945	39.5552	0.8746	17.6367	28.2852	19.9037	42.0077
84	1.4105	8.6393	10.6252	60.0207	0.5967	10.8572	20.0504	0.4732	8.5151	13.0101	8.9456	19.4873

Table A.20 Concentration of trace elements in dry sediments of Lake Moawhitu

LAKE MOAWHITU ($C_{sediments}$)												
Depth (cm)	**Cd (mg/kg)**	**As (mg/kg)**	**Cu (mg/kg)**	**Zn (mg/kg)**	**P(g/kg)**	**Pb (mg/kg)**	**Fe (g/kg)**	**Mn (g/kg)**	**Al (g/kg)**	**Cr (mg/kg)**	**Ni (mg/kg)**	**V (mg/kg)**
1	7.4087	3.7096	74.6932	93.3456	0.8798	5.6218	50.7568	0.6656	40.1582	178.5405	76.2084	138.9786
3	7.7967	3.8152	73.5285	122.0970	1.1383	5.7696	51.0530	0.6273	37.9797	168.6280	74.1626	135.1436
6	7.5023	4.1417	65.9680	90.4732	0.7511	5.4224	49.5569	0.6538	37.0045	169.5385	70.6637	124.4336
9	7.3270	3.8579	64.1985	83.5777	0.7437	5.0840	48.2653	0.6101	35.8956	162.3704	68.7044	126.6027
12	7.1742	3.7864	60.5924	79.1991	0.6964	5.3072	45.9537	0.5925	35.2529	156.3949	67.8085	119.5696
15	7.8976	4.6330	65.7450	89.8903	0.8232	5.7319	48.7479	0.6470	36.1562	166.5604	74.1166	127.1371
18	7.3946	6.0790	64.0792	79.3033	0.8880	5.3470	47.3296	0.6025	35.4871	169.3218	78.8895	128.3705
21	6.9090	5.4217	61.6535	71.7691	0.8554	5.6432	45.1769	0.5630	32.0955	156.5334	72.2648	121.3028
24	7.9845	5.3972	66.6325	83.5876	1.0646	6.0122	48.7167	0.6207	35.7678	178.7542	88.5818	127.2423
27	7.1312	7.2642	60.3951	69.9613	0.8604	6.0876	45.1017	0.4762	29.8727	168.9590	94.6596	115.6132
30	8.2443	7.7413	60.9792	87.2100	0.8944	5.6857	49.9708	0.5079	33.5670	197.6002	112.2053	125.7416
33	5.8349	5.4091	47.4963	59.3732	0.6836	4.0626	39.3872	0.3739	27.3125	150.9247	87.6961	96.6729
39	6.8713	5.2412	51.6584	76.6054	0.7119	5.1689	44.0248	0.4123	33.1374	154.5728	80.1133	113.4895
45	7.1696	4.7764	48.4493	77.2170	0.7160	5.7595	47.6124	0.4285	37.3136	166.7375	79.3321	114.1969
51	6.7500	3.3040	46.1756	79.9761	0.6436	5.2399	42.5199	0.3722	36.0448	154.9759	69.8106	100.3376
57	6.7428	2.6971	45.0998	84.7231	1.2919	2.9648	45.6196	0.3982	25.9247	180.6773	76.4155	97.7970
63	5.5711	3.9062	43.3522	70.1619	0.7940	4.2050	42.7027	0.3850	28.2685	158.9796	75.4555	98.1882
69	6.1282	3.6402	49.6069	74.4562	0.5843	3.8034	47.3446	0.3755	27.0195	190.0765	79.9727	107.0653
75	6.2995	2.0826	46.2098	65.9845	0.5990	2.3507	45.2400	0.3790	24.3235	173.6836	73.3562	97.9457
81	7.3409	2.6328	45.8830	66.4601	0.5875	4.2538	47.3527	0.3438	25.0389	192.9172	81.6684	103.2471

Table A. 21 Concentration of trace elements in dry sediments of F10 and F10 cores collected from Lake Forsyth by previous student as described in section 3.3.6 of chapter 3.

Lake Forsyth Previous core ($C_{sediments}$)												
	F11						F11					
Depth cm	Cd (mg/kg)	As (mg/kg)	Cu (mg/kg)	Zn (mg/kg)	P (mg/kg)	Pb (mg/kg)	Cd (mg/kg)	As (mg/kg)	Cu (mg/kg)	Zn (mg/kg)	P (mg/kg)	Pb (mg/kg)
1	11.3500	5.7621	17.0301	89.0976	1.9177	17.8503	2.2985	1.6889	3.7275	38.7044	0.5323	5.9569
2	1.4727	3.4057	9.9410	71.6424	1.0809	11.4955	0.6224	1.9463	3.7642	36.9110	0.5169	6.0853
3	1.3279	3.0915	9.2641	61.9857	1.0876	12.3556	0.6154	0.8575	3.2886	34.6716	0.4586	5.6539
4	1.3084	3.8518	10.0483	61.9749	1.0078	12.8011	0.6803	1.7607	4.3518	39.4961	0.5132	6.8349
5	1.8429	3.6658	9.4733	57.1488	0.9204	11.9238	0.7347	0.9592	3.8572	37.4700	0.4368	6.0466
7	1.2879	3.9094	8.9586	55.9514	0.7381	10.9076	0.7567	2.0834	5.1692	42.5620	0.5634	8.5483
9	1.5142	4.8852	11.7046	76.3615	0.7331	13.1966	0.7048	2.0926	3.8057	38.4468	0.4650	6.6425
11	1.5481	4.3163	12.6925	74.2688	0.7463	13.9946	0.7054	2.5474	4.7127	41.0131	0.4841	7.3305
13	1.6762	4.9155	12.7691	70.6255	0.7586	14.6995	0.8056	2.2052	4.6622	41.3049	0.4405	6.8648
15	1.4911	4.1236	12.4354	65.7113	0.7170	13.9081	0.8335	2.2973	5.4892	44.1270	0.4582	7.0231
20	1.6607	5.0129	13.1833	72.2723	0.7755	14.7928	0.8972	2.4800	4.6777	37.0688	0.3797	5.0232
25	1.9564	4.4602	11.9210	65.2716	0.7179	13.7862	0.6789	1.3878	4.6925	36.7715	0.3817	4.8353

Appendix B

Enrichment Factors

This appendix presents enrichment factors as described in section 3.4 of chapter 3.

B.1 Enrichment factors

Table B.1 Enrichment factors for Lake Ngāpouri

LAKE NGĀPOURI (EF)						
Depth (cm)	Cd	As	Cu	Zn	P	Pb
1	0.00	0.67	1.53	5.45	4.31	0.37
3	0.26	0.60	1.55	4.72	5.39	0.49
6	0.33	0.85	1.65	2.12	4.66	0.57
9	0.42	0.78	1.63	2.56	5.27	0.67
12	0.34	1.12	1.44	1.39	4.64	0.89
15	0.31	0.99	1.27	1.15	5.76	0.68
18	0.19	0.46	1.01	0.61	2.31	0.66
21	0.17	2.14	1.01	1.04	4.09	0.64
24	0.56	2.14	1.04	1.30	3.97	0.84
27	0.66	1.05	0.67	1.28	6.09	0.60
30	0.48	0.80	0.84	1.31	2.90	0.51
33	0.64	1.24	0.79	1.30	4.49	0.62
39	0.47	1.36	0.84	1.20	4.64	0.60
45	0.56	1.37	0.87	1.28	2.66	0.53
51	0.41	1.15	0.77	0.96	3.06	0.62
57	0.99	1.45	0.65	1.34	6.47	0.71
63	0.83	1.72	0.75	1.26	1.78	0.69

Table B.2 enrichment factors for Lake Tutaeinanga

LAKE TUTAEINANGA (EF)						
Depth (cm)	Cd	As	Cu	Zn	P	Pb
1	2.79	2.79	3.97	2.05	9.10	1.73
2	3.79	3.79	6.14	2.09	7.48	1.92
3	2.58	2.58	5.16	1.71	6.12	1.46
4	2.14	2.14	7.49	1.43	4.53	1.62
5	2.04	2.04	4.05	1.34	4.63	1.57
6	1.83	1.83	2.37	1.13	3.99	1.23
7	1.63	1.63	2.50	0.98	4.07	1.27
8	1.72	1.72	1.93	1.00	4.28	1.27
9	1.98	1.98	1.92	1.16	3.98	1.30
10	1.53	1.53	1.87	0.92	3.14	1.38
11	2.03	2.03	1.77	0.83	3.02	1.32
12	1.24	1.24	1.13	0.88	2.90	0.94
13	1.84	1.84	1.56	0.86	2.67	1.13
14	1.39	1.39	1.05	0.65	2.65	0.90
15	1.15	1.15	1.03	0.59	2.89	0.90
16	1.20	1.20	1.12	0.67	2.78	0.89
17	1.25	1.25	1.04	0.61	2.77	0.88
18	2.53	2.53	2.21	0.96	2.82	1.28
19	1.44	1.44	1.12	0.74	2.85	1.01
20	1.73	1.73	1.09	0.61	2.61	1.03
21	1.92	1.92	1.15	0.76	2.48	1.09
22	1.69	1.69	1.31	1.31	2.29	1.02
23	1.80	1.80	1.09	1.31	2.43	1.04
24	1.98	1.98	0.93	1.03	1.80	0.94
25	3.72	3.72	1.17	1.30	2.29	1.19
26	2.08	2.08	1.09	0.91	2.25	1.18
27	1.53	1.53	0.99	1.12	1.99	1.10
28	1.02	1.02	0.99	0.57	1.89	1.10
29	0.94	0.94	0.82	0.72	1.52	0.97
30	0.92	0.92	0.81	0.68	1.50	0.98
33	1.18	1.18	0.71	0.61	1.22	0.82
36	1.26	1.26	0.72	0.41	1.07	0.80
39	1.28	1.28	0.85	0.97	1.10	0.95
42	2.80	2.80	0.77	0.91	1.21	0.85
45	4.03	4.03	0.89	1.00	1.28	0.88
48	2.53	2.53	0.89	0.95	0.78	0.97
51	6.24	6.24	1.18	1.68	1.24	1.10

Table B.3 Enrichment factors for Lake Forsyth

LAKE FORSYTH (EF)						
Depth (cm)	Cd	As	Cu	Zn	P	Pb
1	0.79	1.91	1.25	1.37	2.52	1.35
3	0.53	2.24	1.20	1.21	1.33	1.07
6	0.62	1.47	1.03	0.99	0.92	1.06
9	0.46	2.26	1.05	1.04	0.98	0.96
12	0.52	1.86	1.07	1.02	0.90	0.76
15	1.07	2.05	1.03	0.97	0.85	0.87
18	0.72	2.49	1.04	1.02	0.89	0.65
21	0.51	1.72	0.88	0.87	0.78	0.57
24	0.91	2.59	1.00	1.03	0.82	0.60
27	0.78	1.00	0.81	1.01	0.91	0.73
30	0.98	1.15	0.99	1.24	1.07	0.94
33	0.74	1.53	0.83	1.00	0.91	0.51
36	1.16	0.76	0.96	1.19	1.07	0.90
39	0.77	1.19	1.04	1.12	1.08	0.94
42	1.44	0.77	1.18	1.41	1.23	0.85
45	1.38	1.10	1.18	1.34	1.24	1.07
48	1.07	1.84	1.13	1.20	1.16	1.13
51	1.29	2.12	1.15	1.24	1.26	1.16
54	0.57	1.14	1.09	1.13	1.14	0.83

Table B.4 Enrichment Factors for Lake Pearson

LAKE PEARSON (EF)						
Depth (cm)	Cd	As	Cu	Zn	P	Pb
1	1.33	1.00	0.56	0.73	1.23	0.88
3	1.23	1.00	0.51	0.65	1.10	0.78
6	1.26	0.97	0.51	0.67	1.16	0.78
9	1.16	1.07	0.48	0.67	1.25	0.72
12	0.95	0.92	0.50	0.63	0.99	0.67
15	1.17	1.09	0.63	0.69	0.99	0.78
18	1.17	0.93	0.55	0.67	0.87	0.75
21	1.51	0.79	0.44	0.69	1.26	0.74
24	1.67	0.95	0.43	0.69	1.81	0.72

Table B.5 Enrichment factors for Lake Heron

LAKE HERON (EF)						
Depth (cm)	**Cd**	**As**	**Cu**	**Zn**	**P**	**Pb**
1	1.41	2.14	0.99	1.00	2.25	1.16
3	1.33	1.40	0.95	1.03	1.49	1.22
6	0.98	1.00	0.94	0.93	0.95	1.11
9	1.06	1.13	1.00	1.27	1.50	1.12
12	1.02	1.19	1.00	1.04	1.27	1.16
15	1.35	1.29	0.96	1.04	1.73	1.17
18	1.09	1.12	1.04	1.09	1.31	1.24
21	1.05	0.88	0.88	0.88	1.02	1.05
24	0.99	0.94	1.11	1.71	1.03	1.15
27	0.93	1.09	1.17	1.20	1.18	1.27
30	1.19	1.09	1.19	1.15	1.31	1.32
36	1.11	1.08	1.17	1.23	1.09	1.17
42	1.45	2.02	1.13	1.12	1.63	1.18
48	1.31	1.76	1.12	1.12	1.31	1.10
54	1.08	0.82	0.95	0.99	0.91	0.98
60	0.79	0.54	0.91	0.98	0.89	0.88
66	0.73	0.63	0.84	0.85	0.76	0.79
72	0.79	0.63	0.87	0.98	0.77	0.85

Table B.6 Enrichment Factors for Lake Moawhitu

LAKE MOAWHITU (EF)						
Depth (cm)	**Cd**	**As**	**Cu**	**Zn**	**P**	**Pb**
1	0.71	0.84	1.00	0.86	0.95	1.03
3	0.79	0.92	1.04	1.19	1.29	1.11
6	0.78	1.02	0.96	0.90	0.88	1.08
9	0.79	0.98	0.96	0.86	0.89	1.04
12	0.79	0.98	0.93	0.83	0.85	1.10
15	0.84	1.17	0.98	0.92	0.98	1.16
18	0.81	1.57	0.97	0.82	1.08	1.11
21	0.83	1.54	1.04	0.83	1.15	1.29
24	0.86	1.38	1.00	0.86	1.28	1.23
27	0.92	2.22	1.09	0.86	1.24	1.50
30	0.95	2.11	0.98	0.96	1.15	1.24
33	0.83	1.81	0.94	0.80	1.08	1.09
39	0.80	1.45	0.84	0.85	0.93	1.14
45	0.74	1.17	0.70	0.76	0.83	1.13
51	0.72	0.84	0.69	0.82	0.77	1.07
57	1.00	0.95	0.94	1.21	2.15	0.84
63	0.76	1.26	0.83	0.92	1.21	1.09

Appendix C: Molar ratios of Mn/Fe, Cu/Pb, Zn/Pb and molar values of Cd and P.

This appendix presents the values for Molar ratios of molar of Mn/Fe, Cu/Pb, Zn/Pb, as described in section 3.6 and number of moles of Cd and P (values used to plot graphs for the molar relationship between Cd and P)

Table C.1 Molar ratios of molar of Mn/Fe, Cu/Pb, Zn/Pb, and number of moles of Cd and P for Lake Ngāpouri

LAKE NGĀPOURI (MOLAR RATIOS)					
Depth (cm)	Mn/Fe	Cu/Pb	Zn/Pb	Cd (moles)	P (moles)
1	0.0159	8.9156	480.7517	0.0006	139.6419
3	0.0137	6.7362	310.7463	0.0171	165.8579
6	0.0161	6.1491	119.9100	0.0163	108.9990
9	0.0191	5.1838	123.0044	0.0214	124.9324
12	0.0182	3.4589	50.4830	0.0180	117.1663
15	0.0158	3.9674	54.6040	0.0144	128.4895
18	0.0199	3.3025	30.2721	0.0111	61.7028
21	0.0205	3.3327	52.2687	0.0076	86.8296
24	0.0140	2.6414	50.0248	0.0245	81.7011
27	0.0119	2.4150	69.3573	0.0410	177.8511
30	0.0073	3.5318	83.6988	0.0265	75.3566
33	0.0080	2.7041	67.3830	0.0294	96.8258
39	0.0089	2.9712	64.4734	0.0265	123.0940
45	0.0096	3.5407	78.6782	0.0252	56.9029
51	0.0098	2.6329	49.9059	0.0353	124.3922
57	0.0113	1.9637	61.0781	0.0580	177.8851
63	0.0059	2.3187	59.0873	0.0445	44.8128
69	0.0063	3.2058	115.9275	0.0748	68.9313
75	0.0024	2.2273	30.3585	0.0738	15.5783
81	0.0046	1.7045	11.1580	0.0500	9.1308

Table C.2 Molar ratios of molar of Mn/Fe, Cu/Pb, Zn/Pb, and number of moles of Cd and P for Lake Tutaeinanga

LAKE TUTAEINANGA (MOLAR RATIOS)					
Depth (cm)	**(Mn/Fe)**	**Cu/Fe**	**Zn/Pb**	**Cd (moles)**	**P (moles)**
1	0.0137	5.8447	0.0023	0.0155	118.0440
2	0.0086	8.1516	0.0011	0.0113	74.5139
3	0.0096	8.9879	0.0011	0.0146	71.2335
4	0.0141	11.7850	0.0012	0.0089	52.0645
5	0.0172	6.5471	0.0026	0.0100	61.1312
6	0.0201	4.9117	0.0041	0.0083	54.9300
7	0.0242	5.0043	0.0048	0.0094	62.1721
8	0.0242	3.8825	0.0062	0.0110	78.6668
9	0.0183	3.7821	0.0048	0.0083	50.0851
10	0.0232	3.4336	0.0068	0.0071	41.1737
11	0.0191	3.4107	0.0056	0.0059	34.8613
12	0.0322	3.0622	0.0105	0.0070	46.3112
13	0.0195	3.5225	0.0055	0.0040	23.8034
14	0.0250	2.9721	0.0084	0.0052	32.6718
15	0.0280	2.9299	0.0095	0.0054	37.4222
16	0.0262	3.2117	0.0082	0.0058	39.6396
17	0.0256	3.0127	0.0085	0.0051	36.4287
18	0.0189	4.3831	0.0043	0.0062	36.7041
19	0.0297	2.8179	0.0106	0.0048	36.0541
20	0.0267	2.7202	0.0098	0.0032	28.7997
21	0.0296	2.6977	0.0110	0.0040	26.4971
22	0.0272	3.2904	0.0083	0.0039	27.5113
23	0.0309	2.6744	0.0115	0.0031	26.1731
24	0.0236	2.5212	0.0094	0.0032	15.1585
25	0.0226	2.5053	0.0090	0.0026	21.7432
26	0.0264	2.3688	0.0111	0.0018	15.9021
27	0.0296	2.2903	0.0129	0.0013	14.6118
28	0.0297	2.2907	0.0130	0.0013	13.7481
29	0.0251	2.1484	0.0117	0.0019	12.9960
30	0.0271	2.0909	0.0130	0.0017	12.4284
33	0.0250	2.1882	0.0114	0.0015	12.5016
36	0.0251	2.2905	0.0109	0.0016	12.6367
39	0.0219	2.2914	0.0096	0.0017	10.7587
42	0.0182	2.3032	0.0079	0.0051	11.1210
45	0.0124	2.5584	0.0049	0.0027	10.8677
48	0.0145	2.3159	0.0063	0.0023	8.2214
51	0.0083	2.7263	0.0030	0.0044	11.6146
54	0.0145	2.8803	0.0050	0.0036	15.9996
57	0.0269	2.2469	0.0120	0.0034	13.3415

Table C.3 Molar ratios of molar of Mn/Fe, Cu/Pb, Zn/Pb, and number of moles of Cd and P for Lake Forsyth.

LAKE FORSYTH (MOLAR RATIOS)					
Depth (cm)	**Mn/Fe**	**Cu/Pb**	**Zn/Pb**	**Cd (moles)**	**P (moles)**
1	0.0113	4.1536	29.3772	0.0113	43.8941
3	0.0080	5.0483	32.6507	0.0084	25.6087
6	0.0079	4.3956	27.0578	0.0116	20.7263
9	0.0084	4.9133	31.4255	0.0075	19.1119
12	0.0092	6.3496	39.0757	0.0088	18.5901
15	0.0076	5.3285	32.2146	0.0151	14.5812
18	0.0077	7.2315	45.5920	0.0106	15.8517
21	0.0097	6.9895	44.5752	0.0092	17.0439
24	0.0100	7.5111	50.0087	0.0147	15.9522
27	0.0098	4.9716	40.1428	0.0121	17.2029
30	0.0110	4.7377	38.0909	0.0130	17.0894
33	0.0106	7.3126	56.3314	0.0124	18.4941
36	0.0113	4.7788	38.0922	0.0163	18.1511
39	0.0119	4.9883	34.6716	0.0117	19.7420
42	0.0116	6.2286	47.7542	0.0200	20.8679
45	0.0118	4.9777	36.5530	0.0179	19.4464
48	0.0142	4.4742	30.5737	0.0160	21.0959
51	0.0122	4.4340	30.7984	0.0167	19.7557
54	0.0165	5.9428	39.4996	0.0082	20.0597
60	0.0125	4.2433	27.6774	0.0139	20.2970
66	0.0118	4.6959	30.1362	0.0220	22.6874
72	0.0145	4.3626	27.7379	0.0164	21.0653
78	0.0133	4.7199	31.5694	0.0173	21.3914
84	0.0140	4.4967	28.1194	0.0192	22.4010

Table C.4 Molar ratios of molar of Mn/Fe, Cu/Pb, Zn/Pb, and number of moles of Cd and P for Lake Pearson.

LAKE PEARSON (MOLAR RATIOS)					
Depth (cm)	**Mn/Fe**	**Cu/Pb**	**Zn/Pb**	**Cd (moles)**	**P (moles)**
1	0.0223	2.2962	10.3853	0.0607	36.9288
3	0.0214	2.3545	10.3555	0.0634	37.2462
6	0.0209	2.3448	10.7098	0.0651	39.5007
9	0.0207	2.3699	11.5313	0.0610	43.1885
12	0.0210	2.6909	11.6826	0.0576	39.2869
15	0.0195	2.8692	11.0349	0.0667	37.2380
18	0.0185	2.6443	11.1828	0.0703	34.4512
21	0.0210	2.1507	11.7129	0.0839	45.9748
24	0.0229	2.1369	12.0827	0.0987	70.0273
27	0.0208	2.4305	11.6180	0.0612	29.6356
30	0.0185	2.8299	11.5125	0.0482	21.8605
33	0.0184	3.1069	11.7599	0.0575	25.0912
36	0.0191	3.1947	11.8722	0.0615	23.4051
39	0.0174	2.7408	10.4181	0.0624	30.8095
42	0.0188	2.9979	11.2129	0.0643	29.2361
48	0.0193	3.0043	11.3625	0.0502	25.4191
54	0.0196	2.8767	10.3440	0.0515	27.6745
60	0.0179	5.2341	15.4081	0.0113	26.7720
66	0.0174	5.1903	15.6845	0.0137	26.6387
72	0.0185	4.8987	15.2527	0.0178	28.4577
78	0.0200	5.0467	15.1134	0.0183	28.5220
84	0.0185	4.7973	14.6198	0.0204	29.6087

Table C. 5 Molar ratios of molar of Mn/Fe, Cu/Pb, Zn/Pb, and number of moles of Cd and P for Lake Heron.

LAKE HERON (MOLAR RATIOS)					
Depth (cm)	**Mn/Fe**	**Cu/Pb**	**Zn/Pb**	**Cd (mol**	**(P-mol)**
1	0.0420	2.6616	13.5169	0.0280	69.2327
3	0.0363	2.4191	13.1968	0.0253	43.9738
6	0.0314	2.6336	12.9888	0.0199	29.8074
9	0.0388	2.7950	17.8030	0.0221	48.5537
12	0.0346	2.6849	13.9663	0.0184	35.5127
15	0.0394	2.5523	13.8917	0.0243	48.0644
18	0.0334	2.6085	13.6991	0.0185	34.6640
21	0.0294	2.6243	13.1681	0.0237	35.8734
24	0.0266	3.0025	23.1006	0.0207	33.3312
27	0.0302	2.8792	14.6806	0.0179	35.3739
30	0.0275	2.8096	13.5740	0.0220	37.4618
36	0.0269	3.1170	16.4013	0.0201	30.6037
42	0.0266	2.9958	14.7953	0.0242	42.1850
48	0.0256	3.1736	15.8286	0.0215	33.1631
54	0.0230	3.0234	15.6699	0.0203	26.4677
60	0.0201	3.2402	17.3445	0.0159	27.7361
66	0.0207	3.3459	16.8773	0.0179	28.7372
72	0.0213	3.1869	17.8777	0.0181	27.1937
78	0.0225	3.0822	14.7226	0.0202	31.4517
84	0.0240	3.1910	17.5198	0.0125	19.2641

Table C.6 Molar ratios of molar of Mn/Fe, Cu/Pb, Zn/Pb, and number of moles of Cd and P for Lake Moawhitu.

LAKE MOAWHITU (MOLAR RATIOS)					
Depth (cm)	**Mn/Fe**	**Cu/Pb**	**Zn/Pb**	**Cd (mol)**	**P (mol)**
1	0.013330696	43.32153	52.6211	0.065907	28.40625
3	0.012489551	41.55394	67.06638	0.069359	36.75122
6	0.013411711	39.66827	52.87781	0.06674	24.25091
9	0.012848293	41.17345	52.09859	0.065181	24.00952
12	0.013105314	37.2266	47.29321	0.063821	22.48482
15	0.013491449	37.39918	49.69989	0.070256	26.57598
18	0.012940779	39.07581	47.00299	0.065782	28.6689
21	0.01266818	35.62315	40.30467	0.061462	27.61846
24	0.012950882	36.13721	44.06089	0.071029	34.37078
27	0.010733202	32.34874	36.42143	0.063439	27.77989
30	0.010332125	34.97026	48.61011	0.07334	28.8762
33	0.00965068	38.12074	46.31649	0.051907	22.07076
39	0.009519965	32.58678	46.96816	0.061126	22.98358
45	0.009148465	27.42865	42.48867	0.06378	23.11519
51	0.008897614	28.73391	48.37114	0.060047	20.77819
57	0.008872072	49.60007	90.56329	0.059984	41.71104
63	0.009164264	33.61594	52.8784	0.04956	25.63599
69	0.008061333	42.52806	62.04086	0.054516	18.86338
75	0.008515576	64.09712	88.95901	0.05604	19.33943
81	0.007379662	35.17049	49.51436	0.065304	18.96686